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COMPLIANCE PLAN

ABERDEEN CHEMICAL PLANT

ABERDEEN, MISSISSIPPI

INTRODUCTION

This Compliance Plan (hereafter "Plan") is being submitted by Conoco Inc. and Vista Polymers Inc. in satisfaction of one of the conditions of the Consent Decree entered in the United States District Court, Northern District of Mississippi (Civil Action No. EC-84-37-NB-D) on August 19, 1985.

The Plan has a fourfold purpose: (1) to describe measures, procedures and equipment already in effect at the plant aimed at reducing, preventing, abating or otherwise controlling emissions of vinyl chloride from equipment in vinyl chloride service; (2) to describe proposed changes in methods and procedures and proposed retraining for plant personnel, aimed at maintaining compliance with the requirements of the National Emission Standard for Hazardous Air Pollutants (NESHAP) for vinyl chloride; (3) to describe proposed equipment revisions for maintaining compliance with the NESHAP requirements for vinyl chloride; (4) to request that certain equivalency modifications be granted.

The Plan provides a sectional review of plant compliance with the NESHAP for vinyl chloride. The Plan includes:

1. Proposed modifications to the plant or its practices are covered under the appropriate sections.

2. Descriptions of pertinent operating and maintenance procedures utilized to ensure compliance with the NESHAP for vinyl chloride or are referenced if previously submitted to EPA.

3. Three requests for equivalency modifications along with pertinent supporting data. These requests concern equipment opening, steam stripping/reactor opening loss and test method 107.

4. A description of plant maintenance and training procedures.

5. A request to approve minor modifications to the Leak Detection and Elimination Plan.

A process description of plant areas which are in vinyl chloride service, including processes installed to assure compliance with the NESHAP, was included in the information submitted under section III. A. of the Consent Decree.

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This document updates compliance plans previously submitted to the EPA dated December 20, 1976 and August 14, 1978.

Plant equipment and procedures as described, and including those modifications proposed in this Plan, will ensure continued compliance with each section of the NESHAP for vinyl chloride.

Nothing in this Plan or its Attachments constitutes an admission, direct or implied, that equipment, methods, procedures, training programs etc. heretofore implemented are or have been insufficient to meet the requirements of the Clean Air Act and/or the regulations governing the emission of vinyl chloride (40 CFR 61 Subpart F).

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COMPLIANCE WITH THE NESHAP

FOR VINYL CHLORIDE

ABERDEEN CHEMICAL PLANT

VISTA POLYMERS INC.

§ 61.64

An owner or operator of a polyvinyl chloride plant shall comply with the requirements of this section and Section 61.65.

(a) Reactor. The following requirements apply to reactors:
(1) The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each reactor is not to exceed 10 ppm, except as provided in paragraph (a)(2) of this section and section 61.65(a).

STATUS OF COMPLIANCE

Vents from the reactors during the charge, polymerization, and recovery/stripping phases of the reactor cycle are routed to the vapor recovery system. This system compresses and condenses the VCM vapors so that they can be recycled. Noncondensible gases collect in the vapor space of the recovered VCM receivers in reactor Module No. 1 and are vented along with a small quantity of VCM to the VCM incinerator where the VCM content is incinerated to less than 10 ppm before being released to the environment.

Emissions from the reactor during the slurry stripping step of the batch cycle are addressed in section 61.64(b).

§ 61.64
(a) Reactor.
(2) The reactor opening loss from each reactor is not to exceed 0.02 g vinyl chloride/kg (0.00002 lb vinyl chloride /lb) of polyvinyl chloride product, with the product determined on a dry solids basis. This requirement applies to any vessel which is used as a reactor or as both a reactor and a stripper. In the bulk process, the product means the gross product of prepolymerization and postpolymerization.

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61.64(a)(2)

STATUS OF COMPLIANCE

The Aberdeen PVC Plant uses a batch suspension polymerization process to produce polyvinyl chloride resin. The polymerization reactors are also used as batch slurry strippers. Following each stripping operation, the reactor/stripper is opened to the atmosphere and the slurry is drained from the reactor.

Compliance with 61.64(a)(2) is currently attained by operating under an equivalency using standard operating procedures to strip the resin to less than 400 ppm vinyl chloride and to purge vinyl chloride from the reactor vapor space to meet the reactor opening loss requirement as described in Section VI of the Compliance Manual submitted to EPA Region IV August 14, 1978. The calculational procedure given in the August 14, 1978 compliance manual is based on the classical mixing equation and using very conservative parameters shows that compliance is achieved via sweeping the vapor space with steam. The existing equivalency is based upon the long-standing recognition by industry and EPA of the technical infeasibility of sampling the reactor/stripper per 61.67(g)(5) for producers stripping in reactors. The continual emission of VCM from the slurry into the reactor vapor space while the slurry is being removed from the reactor makes it impossible to determine the reactor opening loss. The preamble to the October 21, 1976 VCM regulation recognizes this point when it states that vinyl chloride in the resin which has already been stripped to acceptable levels can escape from the resin and become part of the reactor opening loss. The preamble goes on to say that it is not EPA's intent to require additional controls once a resin has been stripped to required levels (41FR46563).

61.64 (a)(2)

STATUS OF COMPLIANCE (Continued)

A research study of reactor opening loss was recently completed at the plant. A summary of this study was submitted to EPA on October 15, 1985. The data generated in this research study supports the current compliance procedure, but this new data now enables the plant to better determine emissions specified in 61.64(a)(2). The research report shows that the reactor opening loss emission from Vista Polymers Inc. reactors' during the stripping operation follows a physical correlation such that the emission can be quantified.

Based on this study, the plant is requesting an equivalency modification to Section 61.67(g)(5) such that the correlation given in the above mentioned research report will be used to determine reactor opening loss. The plant is also requesting that the equivalency modification allow 24-hour averaging of the reactor opening loss emission. The 24-hour averaging of reactor opening loss emissions is the concept used by EPA in the January 9, 1985 Proposed Rule-National Emission Standards for Hazardous Air Pollutants; Vinyl Chloride. This equivalency modification request involves the following sections of the current standard:

61.64(a)(2)	Reactor Opening Loss Emission Limit
61.70(c)(3)	Semiannual Reporting Requirements for Reactor Opening Loss
61.67(g)(5)	Determination of Reactor Opening Loss

61.64(a)(2) (Continued)

STATUS OF COMPLIANCE (Continued)

Equivalency Modification Request for Sections 61.64(a)(2), 61.70(c)(3) and 61.67(g)(5)

The plant requests EPA to grant a modified equivalency for section 61.67(g)(5) such that the quantification of the vinyl chloride reactor opening loss emission from each reactor/stripper opening will be determined per the correlation developed in the above mentioned research report.

The plant also requests EPA to grant a modified equivalency for sections 61.64(a)(2) and 61.70(c)(3) such that compliance and reporting of emissions of vinyl chloride from reactor opening loss will be based on the daily average reactor opening loss.

Compliance will be determined by the following:

> The reactor opening loss shall not exceed 0.02 g vinyl chloride/kg (0.00002 lb vinyl chloride/lb) of polyvinyl chloride product averaged over a 24-hour period, with the product determined on a dry solid basis.

Reporting will be as follows:

> The semiannual report will include the 24-hour average reactor opening loss emission and will be determined by the following equation:

61.64(a)(2) (Continued)

STATUS OF COMPLIANCE (Continued)

$$C = \frac{P_1 \times R_1 \times 10^{-6} + P_2 \times R_2 \times 10^{-6} + \ldots + P_n \times R_n \times 10^{-6}}{Q}$$

Where:

C = 24-hour average reactor opening loss in g(lb) vinyl chloride per kg(lb) polyvinyl chloride product (dry weight basis)

P = dry weight of polyvinyl chloride in reactor from recipe, in kg(lb)

R = reactor opening loss emission for the reactor opening determined from the correlation developed in the above mentioned research study in g(lb) of vinyl chloride per million g(lb) of polyvinyl chloride product (dry weight basis)

n = total number of batches produced during the 24-hour period

Q = total production of resin in the batches produced during the 24-hour period in kg(lb) (dry weight basis)

ADDITIONAL MEANSURES TO BE COMPLETED

Retraining on steam stripping procedures and reactor slurry sampling and handling procedures will be conducted each calendar year. Initial retraining required by the Plan will be completed within 270 days after Plan approval.

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§ 61.64
(a) Reactor.
(3) Manual vent valve discharge: Except for an emergency manual vent valve discharge, there is to be no discharge to the atmosphere from any manual vent valve on a polyvinyl chloride reactor in vinyl chloride service. An emergency manual vent valve discharge means a discharge to the atmosphere which could not have been avoided by taking measures to prevent the discharge. Within 10 days of any discharge to the atmosphere from any manual vent valve, the owner or operator of the source from which the discharge occurs shall submit to the Administrator a report in writing containing information on the source, nature and cause of the discharge,the date and time of the discharge, the approximate total vinyl chloride loss during the discharge, the method used for determining the vinyl chloride loss, the action that was taken to prevent the discharge, and measures adopted to prevent future discharges.

STATUS OF COMPLIANCE

When the vinyl chloride standard was written, industry and plant practice was to use a valve on a reactor or receiver to manually vent inerts to the atmosphere to maintain control. This action was prohibited by section 61.64 (a)(3) except for emergency manual venting. The Aberdeen Chemical Plant has installed incinerators to receive and incinerate the inerts that are generated by the process. No manual venting to the atmosphere is required by the process and it does not occur.

§ 61.64
(b) Stripper. The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each stripper is not to exceed 10 ppm, except as provided in Section 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in Section 61.65(b)(6)(i) before being opened.

STATUS OF COMPLIANCE

Vents from the reactor/stripper during the polymerization and recovery/ steam stripping parts of the reactor batch cycle are routed to the vapor

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61.64 (a)(3) (Continued)

STATUS OF COMPLIANCE (Continued)

recovery system. This system compresses and condenses the VCM vapors so that they can be recycled. Noncondensible gases collect in the vapor space of the recovered VCM receivers in reactor Module No. 1 and are vented along with a small quantity of VCM to the incinerator where the VCM content is incinerated to less than 10 ppm before being released to the environment.

§ 61.64

(c) Mixing, weighing, and holding containers. The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each mixing, weighing, or holding container in vinyl chloride service which precedes the stripper (or the reactor if the plant has no stripper) in the plant process flow is not to exceed 10 ppm, except as provided in Section 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in Section 61.65(b)(6)(i) before being opened.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant does not have any mixing or weighing containers in VCM service. The plant does utilize a number of vinyl chloride storage vessels . These units are:

	No. of Vessels
VCM Storage Bullet*	Two
VCM Storage Sphere	One
Fresh VCM Receiver	Two
Recovered VCM Receiver	Four

*A bullet is a horizontal cylindrical drum designed for pressurized storage.

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61.64(c) (Continued)

STATUS OF COMPLIANCE (Continued)

The sphere and bullets are located in the tank farm. Vents from these vessels are routed to the Emission Recovery System through the dedicated vent header system. This system compresses and condenses the VCM vapors so that they can be recycled. Noncondensible gases from these vents collect in the vapor space of the Module No. 1 recovered VCM receivers. Vents from the Fresh VCM receivers also flow directly to the Module No. 1 recovered VCM receivers. Vents from the Module No. 2 recovered VCM receivers flow to the Module No. 1 recovered VCM receivers. The Module No. 1 recovered VCM receivers are in turn vented to the VCM incinerator where the VCM content is incinerated to less than 10 ppm before being released to the environment.

§ 61.64

(d) Monomer recovery system. The concentration of vinyl chloride in all exhaust gases discharged to the atmosphere from each monomer recovery system is not to exceed 10 ppm, except as provided in Section 61.65(a). This requirement does not apply to equipment that has been opened, is out of operation, and met the requirement in Section 61.65(b)(6)(i) before being opened.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant utilizes three vapor recovery systems. Non-condensible inert gases containing VCM are vented to these units from a number of sources as discussed in other sections of the plan. These units are designed and operated such that these inert gases collect in the vapor space of the Module No. 1 recovered VCM receivers. These collected gases

61.64 (d) (Continued)

are ducted from this system to the VCM incinerator. Continuous venting of inerts from the VCM receivers to the incinerator is not required.

§ 61.64

(e) Sources following the stripper(s). The following requirements apply to emissions of vinyl chloride to the atmosphere from the combination of all sources following the stripper(s) [or the reactor(s) if the plant has no stripper(s)] in the plant process flow including but not limited to, centrifuges, concentrators, blend tanks, filters, dryers, conveyor air discharges, baggers, storage containers, and inprocess wastewater:

(1) In polyvinyl chloride plants using stripping technology to control vinyl chloride emissions, the weighted average residual vinyl chloride concentration in all grades of polyvinyl chloride resin processed through the stripping operation on each calendar day, measured immediately after the stripping operation is completed, may not exceed:

(i) 2000 ppm for polyvinyl chloride dispersion resins, excluding latex resins;

(ii) 400 ppm for all other polyvinyl chloride resins, including latex resins, averaged separately for each type of resin; or

STATUS OF COMPLIANCE

The plant produces polyvinyl chloride by a batch suspension polymerization process. Compliance with section 61.64(e)(1)(ii) is achieved using in-reactor stripping technology to reduce the vinyl chloride content of the stripped slurry averaged over each calendar day to less than 400 ppm vinyl chloride, the product being on a dry weight basis.

Test method 107 or an EPA approved equivalent method will be used to determine the vinyl chloride content of the stripped slurry as follows:

(i) One representative sample of polyvinyl chloride resin will be taken from each batch of resin immediately following

61.64 (e) (Continued)

STATUS OF COMPLIANCE (Continued)

the completion of the stripping operation, and be identified by resin type and grade and date and time the batch was completed. The corresponding quantity of material processed in each stripper will be recorded and identified by resin type and grade and the date and time the batch was completed.

(ii) The quantity of material processed by each reactor/stripper batch on a dry solids basis will be determined using the normal vinyl chloride charge volume for the specific reactor and the calculated conversion of vinyl chloride to polyvinyl chloride for the particular grade of resin produced.

The calculation of the weighted daily average vinyl chloride content of the stripped slurry will be made according to the following equation:

$$A = \frac{P_1M_1 + P_2M_2 + \ldots + P_n M_n}{Q}$$

Where:

A = 24-hour average concentration of vinyl chloride in the stripped slurry on a dry solids basis in ppm.

P = Production of resin represented by the sample, in kg (lb).

M = Concentration of vinyl chloride in one sample of resin, in ppm.

n = Total number of batches of resin produced during the 24-hour period.

Q = Total production of resin over the 24-hour period on a dry solids basis in kg (lb).

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61.64 (e) (Continued)

ADDITIONAL MEASURES TO BE COMPLETED

Retraining on steam stripping procedures and reactor slurry sampling and handling procedures will be conducted each calendar year. Initial retraining required by this Plan will be completed within 270 days after Plan approval.

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(e) Sources following the stripper. (continued)

(2) In polyvinyl chloride plants controlling vinyl chloride emissions with technology other than stripping or in addition to stripping, emissions of vinyl chloride to the atmosphere may not exceed:

(i) 2 g/Kg (0.002 lb/lb) product from the stripper(s) [or reactor(s) if the plant has no stripper(s)] for dispersion polyvinyl chloride resins, excluding latex resins, with the product determined on a dry solids basis;

(ii) 0.4 g/kg (0.0004 lb/lb) product from the strippers [or reactor(s) if the plant has no stripper(s)] for all other polyvinyl chloride resins, including latex resins, with the product determined on a dry solids basis.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant utilizes slurry stripping technology in all of its PVC production. This part of the standard is therefore not applicable.

§ 61.65

An Owner or operator of an ethylene dichloride, vinyl chloride, and/or polyvinyl chloride plant shall comply with the requirements of this section.

(a) Relief valve discharge. Except for an emergency relief discharge, there is to be no discharge to the atmosphere from any relief valve on any equipment in vinyl chloride service. An emergency relief discharge means a discharge which would not have been avoided by taking measures to prevent the discharge. Within 10 days of any relief valve discharge, the owner or operator of the source from which the relief valve discharge occurs shall submit to the Administrator a report in writing containing information on the source, nature and cause of the discharge, the date and time of the discharge, the approximate total vinyl chloride loss during the discharge, the method used for determining the vinyl chloride loss, the action that was taken to prevent the discharge, and measures adopted to prevent future discharges.

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61.65(a) (Continued)

STATUS OF COMPLIANCE

All relief valve discharges from equipment in vinyl chloride service at the plant are reported to the Administrator within ten days of the incident.

The following are items currently in place at the Aberdeen Chemical Plant to prevent relief valve discharges:

1. The pressure, temperature and agitator amperage of each reactor is indicated and recorded in the control room.
2. Each reactor has a high pressure and high temperature alarm that sound in the control room. These alarms must be acknowledged by the panel operator to silence them.
3. The cooling water flow to the jacket and condenser of each reactor is indicated and recorded in the control room.
4. The position of remote operated on-off valves is indicated in the control room.
5. The outside operators and shift supervisors are equipped with a two-way radio and are in constant communication with the panel operators.
6. The outside operators
   a) check reactor rupture discs before each charge to assure they are not ruptured or leaking before the reactor is charged.
   b) monitor and regulate flush water to the reactor agitator seal.
   c) monitor and regulate flush water to the reactor spray nozzle.

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61.65(a) (Continued)

STATUS OF COMPLIANCE (Continued)

7. There is a 24 volt d.c. battery back up system that keeps the control room instrumentation operational during power failures.

8. To prevent an operator from making errors that could result in a runaway reaction or other upset conditions, numerous reactor interlocks which include the following are in place.

   a) An interlock prevents a reactor from being charged if the agitator is not running.

   b) An interlock prevents a reactor from being charged if the agitator is drawing more than no load amps.

   c) An interlock prevents charging the larger formula used in the larger reactors to the smaller reactors in the same module.

   d) A precharge interlock prevents the overcharging of reactors by limiting the amount of charge ingredients that can be included in the charge formula.

9. A severe weather radio is located in the control room and is used to warn operating personnel of approaching storms that could interfere with normal operation.

   a) Plant practice is not to charge reactors during severe thunderstorm conditions because of the possibility of a power outage.

   b) The Shift Supervisor is to kill reactors in the polymerization mode of the cycle if he feels the weather is severe enough that a power failure will likely occur.

10. A very effective polymerization kill system has been developed and installed in the plant which since its installation has killed all reactors in the polymerization cycle in various emergency

61.65(a)(Continued)

STATUS OF COMPLIANCE(Continued)

situations without any reactor relief valve discharges due to uncontrolled pressure buildup. To ensure the operability of the system the following instrumentation and operational checks are conducted on the systems.

a) Each injection pot is equipped with a low pressure alarm which is activated when the pressure is below 250 pounds per square inch.

b) There is a low pressure alarm on the nitrogen supply to the automatic valve actuators which sounds when the pressure in the cylinder is less than 600 pounds per square inch.

c) All the kill pots in a reactor module may be connected with flexible hoses in such a manner to allow the killing agent to be injected manually to a reactor in the module from any injection pot.

d) The injection nozzles on each reactor are checked weekly to assure they are not plugged with polymer buildup.

e) When the ambient temperature is below 20°F, kill agent is injected into each reactor once per shift to assure the injection lines are not frozen.

f) In addition to the checks made by the operator before each reactor batch is charged, an audit of the emergency kill system is conducted weekly.

11. A diesel generator has been installed which is used to power two air compressors to provide instrument air during power failures. The diesel operated generator is operated once per week to ensure reliability.

61.65(a)(Continued)

STATUS OF COMPLIANCE(Continued)

12. Modifications have been made to provide cooling water to each reactor module from the fire water system. This system can be used during power failures to supply cooling water to the reactors. These emergency cooling water pumps are operated once per week to ensure reliability.

13. A chain transfer agent has been developed and is used in the plant. This allows certain molecular weight resins to be produced at lower polymerization pressures. Use of the chain transfer agent allows the plant to operate at lower run pressures on these resins.

14. The pressure rating of the reactors installed in the 1982 expansion is 25 pounds per square inch greater than the previously installed reactors.

15. The operating procedures state a temperature and a pressure at which reactors must be killed.

16. Two high level alarms are installed on each of the fresh vinyl chloride receivers.

17. Rupture disc holders which are assembled and pretorqued in the shop prior to installation have been purchased and installed below all relief valves that are on vessels in vinyl chloride service.

18. Operating procedures require that the vinyl chloride receivers are not filled to greater than 80% of their volume.

19. The material of construction of the rupture discs has been changed to nickel from stainless steel to eliminate the possibility of a premature disc failure caused by chloride stress corrosion cracking.

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61.65(a)(Continued)

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STATUS OF COMPLIANCE(Continued)

20. The plant has a very comprehensive procedure for ordering, inspecting, testing and installing rupture discs. This procedure is included as Attachment A.
21. The settings of all the blowdown rings on all the reactor relief valves have been changed to reduce the likelihood of a relief valve discharge if a rupture disc should fail prematurely.
22. The rupture discs on the reactors are replaced with new discs on an annual basis.
23. The pre-charge agitator amperage is recorded on each reactor batch sheet and must indicate the proper amperage before the batch can be charged.
24. A procedure was developed and is in practice to assure a reactor is empty of liquid before it is charged. Remote controlled cameras are installed to enable the panel operator to conduct the procedure from the control room. If the camera is not functional, an outside operator conducts the procedure.
25. Operators have been and are given disciplinary suspensions for not following established operating procedures.
26. Operating procedures require that the addition of water to the reactors from the catalyst charge pots cannot take place unattended. The outside operator must stay at the water injection control valve when water is being added to the injection pot.
27. A pressure alarm light has been added to the control panel to indicate to the panel operator when there is pressure in the catalyst injection pot.

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61.65(a)(Continued)

STATUS OF COMPLIANCE(Continued)

28. An audible alarm has been added to the control panel which sounds if the catalyst injection pot remains pressurized for longer than normal.
29. The water flush flow rates to the reactor agitator seals and spray nozzles are reduced if for some reason a reactor must contain liquid or slurry for a long period of time.
30. Dual meters are installed for measuring the reactor charge amounts of both vinyl chloride and water.
31. A batch water stripping system with the stripping vessels designed for 150 pounds per square inch has been installed.
32. Thermal relief valves on equipment in vinyl chloride service are ducted to a vinyl chloride containment system.
33. Operators have been instructed on the proper valves to have open during the unloading of vinyl chloride from railroad tank cars to the sphere and a checklist denoting the valve position is filled out before the unloading operation is started.
34. A pressure switch has been added to the vinyl chloride railcar unloading system which automatically shuts down all the unloading compressors on high discharge pressure.
35. Each vinyl chloride unloading compressor has been equipped with an automatic high temperature shutdown switch. The temperature sensor is located on the compression cylinder.
36. Operators have been instructed to have both inlet and outlet valves open on vessels in vinyl chloride service if external heating or steaming is required.

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61.65(a)(Continued)

STATUS OF COMPLIANCE(Continued)

37. A polymerization inhibitor is added to the recovery system seal water system to minimize the polymerization of vinyl chloride in the recovery system.
38. Pressure recorders and high pressure alarms have been added in the control room for monitoring the pressure of the discharge of the recovery system compressors.
39. An instrument air dryer capable of drying the instrument air to a dew point of less than minus 40°F has been installed to serve the vinyl unit.

ADDITIONAL MEASURES TO BE COMPLETED

In addition to the extensive action described above which is more fully explained in our response to Section III.A. of the Consent Decree, listed below are additional items that will be implemented to further minimize the possibility of relief valve discharges.

1.Module No. 2 Blowdown Tank Level Indicator

Inprocess wastewater accumulates in a blowdown tank in Module No. 2 before transfer to the batch water strippers. The blowdown tank is presently equipped with a local level indicator and a high level alarm in the control room. This project will install a level indicator located on the control panel. This new instrumentation will provide the panel operator continuous indication of the blowdown tank level and will reduce the possibility of a relief valve discharge on the vessel due to hydrostatically overfilling with inprocess wastewater.

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61.65(a)(Continued)

The definitive process design for this project will be completed by sixty days after Plan approval. Operations will be informed of the purpose of the new level indicator prior to completion of the project.

Installation of this project will be complete within 300 days after Plan approval.

2.Training

Retraining of vinyl operators on power failure procedures, emergency kill procedures, reactor emptying procedures, cold weather operating procedures, emergency air system procedures and emergency generator system procedures will be conducted each calendar year. Retraining of maintenance employees on rupture disc handling and installation procedures will be conducted each calendar year. Retraining required by this Plan will be completed within 270 days after Plan approval.

§ 61.65

(b) Fugitive emission sources.

(1) Loading and unloading lines: Vinyl chloride emissions from loading and unloading lines in vinyl chloride service which are opened to the atmosphere after each loading or unloading operation are to be minimized as follows:

(i) After each loading or unloading operation and before opening a loading or unloading line to the atmosphere, the quantity of vinyl chloride in all parts of each loading or unloading line that are to be opened to the atmosphere is to be reduced so that the parts combined contain no greater than 0.0038 m^3 (0.13 ft^3) of vinyl chloride, at standard temperature and pressure; and

(ii) Any vinyl chloride removed from a loading or unloading line in accordance with paragraph (b)(1)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in Section 61.66.

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61.65(b)(Continued)

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant receives its supply of VCM in railroad tank-cars. All of the loading and unloading is accomplished using a dedicated system. The tank cars are connected to the unloading system with flexible stainless steel lines. Standard operating procedures have been developed and are followed. These procedures specify that before the hose connections are opened to the atmosphere, the pressure in the unloading lines must be below a specified pressure to ensure that the amount of VCM released is less than 0.13 cubic feet of VCM vapor per hose coupling. The VCM vapor is removed from the unloading lines with the use of the recovery system. The VCM recovered during this process is then sent to the recovered VCM receivers.

ADDITIONAL MEASURES TO BE COMPLETED

Retraining on VCM unloading procedures will be conducted each calendar year. Initial retraining required by this Plan will be completed within 270 days after Plan approval.

§ 61.65
(b) Fugitive emission sources.
(2) Slip Gauges: During loading or unloading operations, the vinyl chloride emissions from each slip gauge in vinyl chloride service are to be minimized by ducting any vinyl chloride discharged from the slip gauge through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in Section 61.66.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant does not utilize slip gauges and no exhaust emissions occur from slip gauges. This section of the standard is therefore not applicable.

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§ 61.65

(b) Fugitive emission sources.

(3) Leakage from pump, compressor, and agitator seals:

(i) Rotating pumps: Vinyl chloride emissions from seals on all rotating pumps in vinyl chloride service are to be minimized by installing sealless pumps, pumps with double mechanical seals, or equivalent as provided in Section 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pump; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in Section 61.66.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant has 13 rotating pumps in vinyl chloride service. These are listed below:

Description	Location
East Bullet Pump	Tank Farm
West Bullet Pump	Tank Farm
North Sphere Pump	Tank Farm
South Sphere Pump	Tank Farm
East VCM Charge Pump	Reactor Module No. 1
West VCM Charge Pump	Reactor Module No. 1
RVCM Charge Pump	Reactor Module No. 1
East Collect Tank Pump	Reactor Module No. 1
West Collect Tank Pump	Reactor Module No. 1
East VCM Charge Pump	Reactor Module No. 2
West VCM Charge Pump	Reactor Module No. 2
East RVCM Charge Pump	Reactor Module No. 2
West RVCM Charge Pump	Reactor Module No. 2

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61.65(b)(3)(i)(Continued)

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STATUS OF COMPLIANCE(Continued)

Nine of the process pumps in vinyl chloride service are located in the Module No. 1 or Module No. 2 reactor areas. These pumps have each been equipped with double mechanical seals. The sealing fluid is high pressure water. The double mechanical seals are operated in such a manner that vinyl chloride emissions from the seals are minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pump.

The remaining four pumps are located in the vinyl chloride unloading area. These pumps are also equipped with double mechanical seals. The sealing fluid is an oil which is contained in a small reservoir above the pump. Circulation is via thermosiphon action. The reservoir is vented to a recovery system.

§ 61.65
(b) Fugitive emission sources.
(3) Leakage from pump, compressor, and agitator seals:
(ii) Reciprocating pumps. Vinyl chloride emissions from seals on all reciprocating pumps in vinyl chloride service are to be minimized by installing double outboard seals, or equivalent as provided in Section 61.66. If double outboard seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pumps; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in Section 61.66.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant does not have any reciprocating pumps in VCM service. This part of the VCM emission standard is therefore not applicable.

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§ 61.65

(b) Fugitive emission sources.

(3) Leakage from pump, compressor, and agitator seals:

(iii) Rotating compressor: Vinyl chloride emissions from seals on all rotating compressors in vinyl chloride service are to be minimized by installing compressors with double mechanical seals, or equivalent as provided in Section 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the compressor; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in Section 61.66.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant utilizes rotating compressors in the handling of VCM vapor streams. These units in VCM service are:

Description	No. in Service	Location
Vacuum Pump	Two	Emission Recovery System
Recovery Compressor	Two	Emission Recovery System
Vacuum Pump	Two	Reactor Module No. 1 Recovery System
Recovery Compressor	Two	Reactor Module No.1 Recovery System
Vacuum Pump	Two	Reactor Module No. 2 Recovery System
Recovery Compressor	Three	Reactor Module No. 2 Recovery System

Each of these compressors is equipped with double mechanical seals. The double mechanical seals are operated in such a manner that vinyl chloride emissions from the seals are minimized by maintaining the pressure between the two seals so that any leak that occurs is into the compressor.

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§ 61.65
(b) Fugitive emission sources.
(3) Leakage from pump, compressor, and agitator seals:
(iv) Reciprocating compressors: Vinyl chloride emissions from seals on all reciprocating compressors in vinyl chloride service are to be minimized by installing double outboard seals or equivalent as provided in Section 61.66. If double outboard seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the compressor; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in Section 61.66.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant uses five reciprocating compressors for unloading railcars. These compressors are equipped with an enclosed seal area, commonly referred to as a "double distance piece". The seal space is vented to the emission recovery system. Leakage through these seals is therefore vented to a closed process system.

§ 61.65
(b) Fugitive emission sources.
(3) Leakage from pump, compressor, and agitator seals:
(v) Agitator: Vinyl chloride emissions from seals on all agitators in vinyl chloride service are to be minimized by installing agitators with double mechanical seals or equivalent as provided in Section 61.66. If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the agitated vessel; by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in Section 61.66.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant has an agitator on each of the PVC reactors. Each agitator is equipped with a double mechanical seal. The double mechanical seals are operated in such a manner that vinyl chloride emissions are minimized by maintaining the pressure between the two seals so that any leak that occurs is into the vessel.

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§ 61.65

(b) Fugitive emission sources.

(4) Leakage from relief valves: Vinyl chloride emissions due to leakage from each relief valve on equipment in vinyl chloride service are to be minimized by installing a rupture disk between the equipment and the relief valve, by connecting the relief valve discharge to a process line or recovery system or equivalent as provided in Section 61.66.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant utilizes relief valves to protect equipment from overpressure conditions. Relief valves on equipment in VCM service are either tied into collection headers or have rupture discs placed under them.

Emissions from relief valves tied into collection headers are routed either to a VCM storage vessel or to the emission recovery system.

§ 61.65

(b) Fugitive emission sources

(5) Manual venting of gases: Except as provided in § 61.64(a)(3), all gases which are manually vented from equipment in vinyl chloride service are to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm; or equivalent as provided in Section 61.66.

STATUS OF COMPLIANCE

Operating procedures prohibit the venting of gases from equipment in vinyl chloride service directly to the atmosphere. Vents are routed to either the reactor recovery or emission recovery systems. These units compress and condense the VCM vapors so that they can be recycled. Noncondensible gas collects in the vapor space of the recovered VCM receiver and is vented along with a small quantity of VCM to the incinerator where the VCM is incinerated to less than 10 ppm before being released to the environment.

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§ 61.65

(b) Fugitive emission sources

(6) Opening of equipment: Vinyl chloride emissions from opening of equipment (including loading or unloading lines that are not opened to the atmosphere after each loading or unloading operation) are to be minimized as follows:

(i) Before opening any equipment for any reason, the quantity of vinyl chloride is to be reduced so that the equipment contains no more than 2.0 percent by volume vinyl chloride or 0.0950 m^3 (25 gal) of vinyl chloride, whichever is larger at standard temperature and pressure; and

(ii) Any vinyl chloride removed from the equipment in accordance with paragraph (b)(6)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in Section 61.66.

STATUS OF COMPLIANCE

The vinyl chloride content of equipment that can contain more than 0.0950 m^3 (25 gal) of vinyl chloride at standard temperature and pressure is reduced to below 2.0 percent by volume by one of the following methods.

1. Vinyl chloride in equipment is ducted to a recovery system and steam is added at the same time to purge the equipment for a minimum of 15 minutes or the pressure in the equipment is reduced to a level such that the equipment contains less than 25 gallons of vinyl chloride at standard temperature and pressure.
2. Vinyl chloride is displaced with water and the water is then stripped in the vessel to below 10 ppm vinyl chloride or is routed to the batch water stripping system.

ADDITIONAL MEASURES TO BE COMPLETED

Retraining on equipment opening procedures will be conducted each calendar year. Initial retraining as required by this Plan will be completed within 270 days of Plan approval.

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§ 61.65
(b) Fugitive emission sources.
(7) Samples: Unused portions of samples containing at least 10 percent by weight vinyl chloride are to be returned to the process, and sampling techniques are to be such that sample containers in vinyl chloride service are purged into a closed process system.

STATUS OF COMPLIANCE

Samples are collected on a nonroutine basis from the PVC polymerization reactors prior to stripping . These samples are taken to inspect the quality of the PVC formed during polymerization. The VCM content of these samples is reduced to less than 10 percent by pulling a vacuum on the sample container with the Emission Recovery System. The VCM recovered from the sample is returned to the process by the recovery system.

Samples of other streams containing greater than 10 percent VCM are periodically taken. These are usually associated with special engineering studies or are used to confirm the quality of raw materials. Sampling procedures are established at the time of the studies and all unused portions of these samples are returned to the process.

All other samples taken by the plant are taken from process streams containing less than 10 percent VCM.

§ 61.65
(b) Fugitive emission sources.
(8) Leak detection and elimination: Vinyl chloride emissions due to leaks from equipment in vinyl chloride service are to be minimized by instituting and implementing a formal leak detection and elimination program. The owner or operator shall submit a description of the program to the Administrator for approval. The program is to be submitted within 45 days of the effective date of these regulations, unless a waiver of compliance is granted under Section 61.11. If a waiver of compliance is granted, the program is to be submitted on a date scheduled by the Administrator. Approval of a program will be granted by the Administrator provided he finds:

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61.65(b)(8)(Continued)

(i) It includes a reliable and accurate vinyl chloride monitoring system for detection of major leaks and identification of the general area of the plant where a leak is located. A vinyl chloride monitoring system means a device which obtains air samples from one or more points on a continuous sequential basis and analyzes the samples with gas chromatorgraphy or, if the owner or operator assumes that all hydrocarbons measured are vinyl chloride, with infared spectrophotometry, flame ion detection, or an equivalent or alternative method.

(ii) It includes a reliable and accurate portable hydrocarbon detector to be used routinely to find small leaks and to pinpoint the major leaks indicated by the vinyl chloride monitoring system. A portable hydrocarbon detector means a device which measures hydrocarbons with a sensitivity of at least 10 ppm and is of such design and size that it can be used to measure emissions from localized points.

(iii) It provides for an acceptable calibration and maintenance schedule for the vinyl chloride monitoring system and portable hydrocarbon detector. For the vinyl chloride monitoring system, a daily span check is to be conducted with a concentration of vinyl chloride equal to the concentration defined as a leak according to paragraph (b)(8)(vi) of this section.

The calibration is to be done with either:
(A) A calibration gas mixture prepared from gases specified in section 5.2.1 and 5.2.2 of Test Method 106 and in accordance with section 7.1 of Test Method 106, or

(B) A calibration gas cylinder standard containing the appropriate concentration of vinyl chloride. The gas composition of calibration gas cylinder standard is to have been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life of each cylinder so that the concentration does not change greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the manufacturer to the buyer. If a gas chromatograph is used as the vinyl chloride monitoring system, these gas mixtures may be directly used to prepare a chromatograph calibration curve as described in section 7.3 of Test Method 106. The requirements in section 5.2.3.1 and 5.2.3.2 of Test Method 106 for certification of cylinder standards and for establishment and verification of calibration standards are to be followed.

(iv) The location and number of points to be monitored and the frequency of monitoring provided for in the program are acceptable when they are compared with the number of pieces of equipment in vinyl chloride service and the size and physical layout of the plant.

(v) It contains an acceptable plan of action to be taken when a leak is detected.

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61.65(b)(8)(Continued)

(vi) It contains a definition of leak which is acceptable when compared with the background concentrations of vinyl chloride in the areas of the plant to be monitored by the vinyl chloride monitoring system. Measurements of background concentrations of vinyl chloride in the areas of the plant to be monitored by the vinyl chloride monitoring system are to be included with the description of the program. The definition of leak for a given plant may vary among the different areas within the plant and is also to change over time as background concentrations in the plant are reduced.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant submitted the Leak Detection and Elimination Plan to Region IV of the Environmental Protection Agency on May 16, 1977. Approval of this plan was granted on June 30, 1977. Since this time, the plan has been revised and approved several times. These are listed below.

DATE OF SUBMITTAL OF PROPOSED REVISION	REQUEST SUBMITTED TO	DATE OF APPROVAL FROM AGENCY
April 6, 1979	EPA Region IV	July 6, 1979
November 21, 1979	EPA Region IV	December 17, 1979
August 15, 1983	Mississippi DNR	August 23, 1983

The plant follows the approved Leak Detection and Elimination Plan. There are five minor modifications to the previously approved Leak Detection and Elimination Plan which the plant is requesting the EPA to approve at this time. These are as follows:

1) The analysis cycle time for the Honeywell chromatographic column has been changed from 60 seconds to 70 seconds to improve sample resolution.

2) The oven temperature for the Honeywell chromatographic column has been changed from 60°C to 80°C to improve sample resolution.

3) The automatic sample injection of standard gases feature on the gas chromotographs is no longer used. Manual standard gas injection is used.

4) When the 1979 plan was submitted, there were three HNU portable hydrocarbon detectors in the plant. The calibration procedure called for storing checked and calibrated machines in the guardhouse and one for use

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61.65(b)(8)(Continued)

STATUS OF COMPLIANCE(Continued)

in the vinyl area. Once per week, the monitor in the vinyl area was taken to the guardhouse and exchanged for a machine that had been checked and calibrated. Now the plant has eight HNU portable hydrocarbon detectors in the plant. The current calibration frequency for each dectector is at least once every two weeks regardless of the number of detectors in the plant.

5) The leak detection form that was used in the 1979 submittal has been changed to allow recording more than one leak per page. A copy of the form is attached: (Attachment B)

ADDITIONAL MEASURES TO BE COMPLETED

Retraining on the Leak Detection and Elimination Plan will be conducted on an annual basis. Initial retraining required by this Plan will be completed within 270 days of Plan approval.

To further reduce the possibility of leaks, the plant proposes to install a new type of valve position indicator on selected valves. The current position indicator is mounted on the valve operator, not the valve. Thus if the coupling between the operator and the valve fails, a false indication of the valve position may be provided. In addition, the magnetic portion of the valve indicator assembly is not securely fastened to the assembly.

The plant has consulted with a limit switch manufacturer and in conjunction with the manufacturer developed a new design whereby a standard proximity switch can be used to provide positive indication of the valve stem rather than the actuator position. The design involves the use of a standard proximity switch with a custom designed indicator bracket. One unit has been tested in the shop and then installed in the field. The performance

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61.65(b)(8)(Continued)

ADDITIONAL MEANSURES TO BE COMPLETED (Continued)

on this test unit has been favorable. This new type valve indicator will be installed on 70 valves that have been identified as having the highest potential for causing a leak to the atmosphere based on the type of service or history of leaks.

This project will greatly reduce the possibility of accidental leakage to the atmosphere due to valve position switch indicator failure.

The definitive process design for this project will be completed by sixty days after Plan approval. Operations will be informed of the operational aspects of this project prior to installation.

Installation of this project will be complete within 300 days after Plan approval.

§ 61.65

(b) Fugitive emission sources.

(9) Inprocess wastewater: Vinyl chloride emissions to the atmosphere from inprocess wastewater are to be reduced as follows:

(i) The concentration of vinyl chloride in each inprocess wastewater stream containing greater than 10 ppm vinyl chloride measured immediately as it leaves a piece of equipment and before being mixed with any other inprocess wastewater stream is to be reduced to no more than 10 ppm by weight before being mixed with any other inprocess wastewater which contains less than 10 ppm vinyl chloride; before being exposed to the atmosphere; before being discharged to a wastewater treatment process; or before being discharged untreated as a wastewater. This paragraph does apply to water which is used to displace vinyl chloride from equipment before it is opened to the atmosphere in accordance with Section 61.64(a)(2) or paragraph (b)(6) of this section, but does not apply to water which is used to wash out equipment after the equipment has already been opened to the atmosphere in accordance with Section 61.64(a)(2) or paragraph (b)(6) of this section.

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61.65(b)(9)(Continued)

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STATUS OF COMPLIANCE

The plant has made several significant improvements to the inprocess wastewater stripping system since the preparation of the August 14, 1978 Compliance Manual. At that time there was one water stripping vessel in each reactor module that collected and stripped the water from VCM contaminated sources. The pressure rating of the stripping vessel in the Module No. 1 was derated after a pressure vessel inspection, which made replacement of the vessel necessary. The decision was made to install a set of two batch water strippers in Module No. 1 to handle stripping of all VCM contaminated water in the plant. Each stripper would alternate between being a collector and a stripper. The installation of this system was complete in 1981. A compliance test took place on July 29, 1981 with Mr. Joe Riley of Environmental Protection Agency Region IV observing. An additional improvement was completed in 1984 when the Emission Recovery System vacuum pumps and compressors were replaced. This improved the capacity of the emission recovery system as the old vacuum pumps and compressors were not delivering rated capacity due to wear.

ADDITIONAL MEASURES TO BE COMPLETED

In order to further ensure that process water is stripped to required levels, a pressure and temperature recorder will be installed on the batch water strippers. Currently, temperature and pressure are indicated, but if a process upset causes the system pressure to increase briefly during the stripping operation, the operator may not notice the pressure increase. The current proven stripping procedure is to hold the batch water stripper at specified temperature and pressure limits for a specified time. This

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61.65(b)(9)(i)(Continued)

ADDITIONAL MEASURES TO BE COMPLETED (Continued)

recorder will document whether the pressure limitation has been exceeded during the critical stripping period. The operating procedures will call for a batch to be restripped if abnormalities are observed in the pressure and temperature history of the batch.

The definitive process design for this project will be completed by sixty days after Plan approval.

Installation of this project will be complete within 300 days after Plan approval.

Retraining on wastewater stripping procedures will be conducted each calendar year. Initial retraining required by this Plan will be completed within 270 days of Plan approval.

61.65
(b) Fugitive emission sources.
(9) Inprocess wastewater
(ii) Any vinyl chloride removed from the inprocess wastewater in accordance with paragraph (b)(9)(i) of this section is to be ducted through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm, or equivalent as provided in Section 61.66.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant routes all vapor emissions from the water strippers to the Emission Recovery System or the main recovery systems. These units compress and condense the VCM vapors for recycle to the process. Noncondensible gases collect in the vapor space of the recovered VCM receivers and are vented along with a small quantity of VCM to the incinerator where the VCM is incinerated to less than 10 ppm before being released to the environment.

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§ 61.65

(c) The requirements in paragraphs (b)(1), (b)(2), (b)(5), (b)(6), (b)(7) and (b)(8) of this section are to be incorporated into a standard operating procedure and made available upon request for inspection by the Administrator. The standard operating procedure is to include provisions for measuring the vinyl chloride in equipment $4.75m^3$ (1,250 gal) in volume for which an emission limit is prescribed in Section 61.65(b)(6)(i) prior to opening the equipment and using Test Method 106, a portable hydrocarbon detector, or an equivalent or alternative method. The method of measurement is to meet the requirements of Section 61.67(g)(5)(i)(A) or (g)(5)(i)(B).

STATUS OF COMPLIANCE

Loading and Unloading Lines [61.65(b)(1)]

Standard operating procedures for unloading of vinyl chloride monomer including procedures that ensure compliance with section 61.65(b) are available at the plant.

Slip Gauges [61.65(b)(2)]

The plant does not utilize slip gauges and therefore standard operating procedures are not applicable.

Manual Venting of Gases [61.65(b)(5)]

As explained under status of compliance for 61.65(b)(5), vents from equipment in vinyl chloride service are routed to a recovery system. The vapors from the recovery system are compressed, condensed and routed to the recovered VCM receivers. Inerts from the receivers are routed to the incinerator. Standard operating procedures prohibit manual venting of equipment in vinyl chloride service and are available at the plant.

Opening of Equipment [61.65(b)(6)]

Before opening equipment which contains more than 25 gallons of vinyl chloride at standard temperature and pressure, the procedures given under status of compliance for 61.65(b)(6)(i) are followed. The plant has the

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61.65(c) (Continued)

STATUS OF COMPLIANCE (Continued)

following vessels that are larger than 1,250 gallons in vinyl chloride service.

Vessel	Number
Storage Sphere	1
Storage Bullet	2
Fresh VCM Receivers	2
Recovered VCM Receivers	4
Wastewater Receiving/Stripping Vessels	3
New Module Recovery Knockout Pots	2

Before opening these vessels, vinyl chloride is either displaced with water and the water is then stripped to less than 10 ppm vinyl chloride or the vessel is steam stripped and recovered. The standard requires Test Method 106, a portable hydrocarbon detector or an equivalent or alternative method be used to measure the vinyl chloride in equipment greater than 1250 gallons prior to opening. Vista is requesting an equivalency to using Test Method 106 or a portable hydrocarbon detector due to technical problems when trying to use one of these two methods with the equipment full of water or having just been steamed.

If water displacement is used, the vessel is liquid full after the VCM has been removed from the vessel. Neither Test Method 106 or a portable hydrocarbon detector are suitable for determining the VCM content of water.

If steam purge is used to clear the vessel, the vessel contains water vapor and trace quantities of VCM after completion of the steam purge. When

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61.65(c)(Continued)

STATUS OF COMPLIANCE(Continued)

sampling is done using Test Method 106, the steam in the sample condenses resulting in an erroneous VCM concentration. A portable hydrocarbon detector cannot be used because the lack of oxygen and high water vapor content affect the instruments calibration and any condensed water can mechanically damage the instrument.

Equivalency Modification Request for section 61.65(c)

The plant requests EPA to grant a modified equivalency for section 61.65(c) such that the following two methods can be used to measure the vinyl chloride content in equipment prior to opening:

1. If vessels are completely filled with water, VCM emissions from the vessel will be determined by measuring the VCM content of a representative sample of water. The VCM content of the water shall be determined by test method 107 or an EPA approved equivalent method.

2. If the vessel has been steam purged, the VCM emissions will be calculated from the partial pressure of VCM in the vessel vapor space as follows:

A. The partial pressure (mmHg) of vinyl chloride in the vessel vapor space will be determined from:

$$PPVC = 760 - VV - VPW$$

Where:

PPVC = partial pressure of vinyl chloride in mmHg.

760 = atmospheric pressure at 0°C, in mmHg.

VV = absolute value of vessel vacuum in mmHg.

VPW = vapor pressure of water in mmHg at the vessel temperature.

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61.65(c)(Continued)

STATUS OF COMPLIANCE(Continued)

B. The vessel vapor space volume(m^3) will be determined from dimensions of the vessel.

C. The vessel opening loss VCM emission (kg) will be determined by the following equation:

$$VOL = \frac{(PPVC)\ (VSV)\ \ (1.002)}{(273 + VT)}$$

Where:

PPVC = Partial pressure of vinyl chloride in mm Hg.

VSV = Vessel vapor volume in m^3.

1.002 = Ideal gas constant for vinyl chloride

VOL = Kg of VCM released.

VT = Vessel Temperature in °C.

Samples [61.65(b)(7)]

Sampling procedures for sampling reactors prior to stripping are available at the plant. Sampling procedures for special tests are developed for the specific test as required.

Leak Detection and Elimination Plan [61.65(b)(8)]

The approved Leak Detection and Elimination Plan is available at the plant.

§ 61.66 Equivalent Equipment and Procedures.

Upon written application from an owner or operator, the Administrator may approve use of equipment or procedures which have been demonstrated to his satisfaction to be equivalent in terms of reducing vinyl chloride emissions to the atmosphere to those prescribed for compliance with a specific paragraph of this subpart. For an existing source, any request for using an equivalent method as the initial measure of control is to be submitted to the Administrator within 30 days of the effective date. For a new source, any request for using an equivalent method is to be submitted to the Administrator with the application for approval of construction of modification required by Section 61.07.

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61.66 Equivalent Equipment and Procedures(Continued)

STATUS OF COMPLIANCE

In this compliance Plan, equivalency modifications for sections 61.64(a)(2), 61.65(c), 61.67(g)(5), 61.70(c)(3), and EPA method 107 are requested.

§ 61.67 Emission Tests.

(a) Unless a waiver of emission testing is obtained under Section 61.13, the owner or operator of a source to which this subpart applies shall test emissions from the source,

(1) Within 90 days of the effective date in the case of an existing source or a new source which has an initial startup date preceding the effective date, or

(2) Within 90 days of startup in the case of a new source, initial startup of which occurs after the effective date.

STATUS OF COMPLIANCE

An initial emission test was conducted during the period September 26 to September 28, 1978 and a test report was sent to EPA Region IV on October 25, 1978. Since this time, the following emission tests have been conducted and reports submitted.

Equipment	Date of Test	Date of Report	Report Submitted To
Batch Water Strippers	July 29, 1981	August 19, 1981	EPA Region IV
D-700 Reactor	June 8-10, 1982	June 21, 1982	Mississippi DNR
D-745 Reactor	March 9-10, 1982	April 7, 1982	Mississippi DNR
Spare Inert Vent Incinerator	September 1-3, 1982	October 1, 1982	Mississippi DNR

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61.67 Emission tests.
(b) The owner or operator shall provide the Administrator at least 30 days prior notice of an emission test to afford the Administrator the opportunity to have an observer present during the test.

STATUS OF COMPLIANCE

Notice of emission testing is given at least 30 days prior to the emission test.

61.67 Emission tests.
(c) Any emission test is to be conducted while the equipment being tested is operating at the maximum production rate at which the equipment will be operated and under other relevant conditions as may be specified by the Administrator based on representative performance of the source.

STATUS OF COMPLIANCE

Production information is given for periods of time covering emission testing.

61.67 Emission tests.
(d) [Reserved]

61.67 Emission tests.
(e) When at all possible, each sample is to be analyzed within 24 hours, but in no case in excess of 72 hours of sample collection. Vinyl chloride emissions are to be determined within 30 days after the emission test. The owner or operator shall report the determinations to the Administrator by a registered letter dispatched before the close of the next business day following the determination.

STATUS OF COMPLIANCE

During emission testing, samples are analyzed within 24 hours when at all possible, but no later than 72 hours after sample collection. Results are reported in a timely fashion.

61.67 Emission tests.
(f) The owner or operator shall retain at the plant and make available, upon request, for inspection by the Administrator, for a minimum of 2 years records of emission test results and other data needed to determine emissions.

STATUS OF COMPLIANCE

Emission test results and records are retained for a minimum of two years.

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61.67 Emission tests.

(g) Unless otherwise specified, the owner or operator shall use test Test Methods in Appendix B to this part for each test as required by paragraphs (g)(1), (g)(2), (g)(3), (g)(4), and (g)(5) of this section, unless an equivalent method or an alternative method has been approved by the Administrator. If the Administrator finds reasonable grounds to dispute the results obtained by an equivalent or alternative method, he may require the use of a reference method. If the results of the reference and equivalent or alternative methods do not agree, the results obtained by the reference method prevail, and the Administrator may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn. Whenever Test Method 107 is specified, and the conditions in Section 1.1, "Applicability" of Method 107A are met, Method 107A may be used.

(1) Test Method 106 is to be used to determine the vinyl chloride emissions from any source for which an emission limit is prescribed in Section 61.62(a) or (b) Section 61.63(a), or Section 61.64(a)(1),(b),(c), or (d), or from any control system to which reactor emissions are required to be ducted in Section 61.64 (a)(2) or to which fugitive emissions are required to be ducted is Section 61.65(b)(1)(ii), (b)(2), (b)(5), (b)(6)(ii), or (b)(9)(ii).

(i) For each run, one sample is to be collected. The sampling site is to be at least two stack or duct diameters downstream and one half diameter upstream from any flow disturbance such as a bend, expansion, contraction, or visible flame. For a rectangular cross section an equivalent diameter is to be determined form the following equation:

equivalent diameter=2 (length) (width)/length+width

The sampling point in the duct is to be at the centroid of the cross section. The sample is to be extracted at a rate proportional to the gas velocity at the sampling point. The sample is to be taken over a minimum of one hour, and is to contain a minimum volume of 50 liters corrected to standard conditions.

(ii) Each emission test is to consist of three runs. For the purpose of determining emissions, the average of results of all runs is to apply. The average is to be computed on a time weighted basis.

(iii) For gas streams containing more than 10 percent oxygen the concentration of vinyl chloride as determined by Test Method 106 is to be corrected to 10 percent oxygen (dry basis) for determination of emissions by using the following equation:

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61.67(g) (Continued)

$C_{b(corrected)} = C_b$ 10.9/20.9-percent O_2

Where:

$C_{b\ (corrected)}$=The concentration of vinyl chloride in the exhaust gases, corrected to 10-percent oxygen.

C_b=The concentration of vinyl chloride as measured by Test Method 106.

20.9=Percent oxygen in the ambient air at standard conditions.

10.9=Percent oxygen in the ambient air at standard conditions, minus the 10.0 percent oxygen to which the correction is being made.

Percent O_2=Percent oxygen in the exhaust gas as measured by Reference Method 3 in Appendix A of Part 60 of this chapter.

(iv) For those emission sources where the emission limit is proscribed in terms of mass rather than concentration, mass emissions in kg/100 kg product are to be determined by using the following equation:

$C_{ax} = [C_b(2.60)\ Q\ 10^{-6}]\ [100]/Z$

Where:

C_{ax}=kg vinyl chloride/100 kg product.

C_b= The concentration of vinyl chloride as measured by Test Method 106.

2.60=Density of vinyl chloride at one atmosphere and 20° C in kg/m^3.

Q=Volumetric flow rate in m^3/hr as determined by Reference Method 2 of Appendix A to Part 60 of this chapter.

10^{-6}=Conversion factor for ppm.

Z=Production rate (kg/hr).

STATUS OF COMPLIANCE

Compliance with section 61.67(g)(1) is described under status of compliance with section 61.67(a).

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61.67(g)(Continued)

(2) Test Method 107 is to be used to determine the concentration of vinyl chloride in each inprocess wastewater stream for which an emission limit is prescribed in Section 61.65(b)(9)(i).

STATUS OF COMPLIANCE

Compliance with section 61.67(g)(2) is described under status of compliance with section 61.67(a).

(3) Where a stripping operation is used to attain the emission limit in Section 61.64(e), emissions are to be determined using Test Method 107 as follows:

(i) The number of strippers and samples and the types and grades of resin to be sampled are to be determined by the Administrator for each individual plant at the time of the test based on the plant's operation.

(ii) Each sample is to be taken immediately following the stripping operation.

(iii) The corresponding quantity of material processed by each stripper is to be determined on a dry solids basis and by a method submitted to and approved by the Administrator.

(iv) At the prior request of the Administrator, the owner or operator shall provide duplicates of the samples required in paragraph(g)(3)(i) of this section.

STATUS OF COMPLIANCE

Compliance with section 61.67(g)(3) is described under status of compliance with section 61.67(a).

(4) Where control technology other than or in addition to a stripping operation is used to attain the emission limit in Section 61.64(e), emissions are to be determined as follows:

(i) Test Method 106 is to be used to determine atmospheric emissions from all of the process equipment simultaneously. The requirements of paragraph (g)(1) of this section are to be met.

(ii) Test Method 107 is to be used to determine the concentration of vinyl chloride in each inprocess wastewater stream subject to the emission limit prescribed in Section 61.64(e). The mass of vinyl chloride in kg/100 kg product in each inprocess wastewater stream is to be determined by using the following equation:

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61.67(g)(Continued)

$$C_{bx} = [C_d R 10^{-6}] [100]/Z$$

Where:
C_{bx} = kg vinyl chloride/100 kg product.
C_d = the concentration of vinyl chloride as measured by Test Method 107.
R = water flow rate in l/hr, determined in accordance with a method which has been submitted to and approved by the Administrator.
10^{-6} = Conversion factor for ppm.
Z = Production rate (kg/hr), determined in accordance with a method which has been submitted and approved by the Administrator.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant uses in-reactor stripping technology to control emissions specified in 61.64(e) and therefore the requirements listed in 61.64(g)(4) are not applicable.

(5) The reactor opening loss for which an emission limit is prescribed in Section 61.64 (a)(2) is to be determined. The number of reactors for which the determination is to be made is to be specified by the Administrator for each individual plant at the time of the determination based on the plant's operation. For a reactor that is also used as a stripper, the determination may be made immediately following the stripping operation.

(i) Except as provided in paragraph (g)(5)(ii) of this section, the reactor opening loss is to be determined using the following equation:

$$C=W(2.60)\ (10^{-6})\ (Cb)/YZ$$

Where:
C = kg vinyl chloride emissions/kg product.
W = Capacity of the reactor in m^3.
2.60 = Density of vinyl chloride at one atmosphere and 20° C in kg/m^3.
10^{-6} = Conversion factor for ppm.
C_b = ppm by volume vinyl chloride as determined by Test Method 106 or a portable hydrocarbon detector which measures hydrocarbons with a sensitivity of at least 10 ppm.
Y = Number of batches since the reactor was last opened to the atmosphere.
Z = Average kg of polyvinyl chloride produced per batch in the number of batches since the reactor was last opened to the atmosphere.

61.67(g)(Continued)

(A) If Method 106 is used to determine the concentration of vinyl chloride (Cb), the sample is to be withdrawn at a constant rate with a probe of sufficient length to reach the vessel bottom from the manhole. Samples are to be taken for 5 minutes within 6 inches of the vessel bottom, 5 minutes near the vessel center, and 5 minutes near the vessel top.

(B) If a portable hydrocarbon detector is used to determine the concentration of vinyl chloride (Cb), a probe of sufficient length to reach the vessel bottom from the manhole is to be used to make the measurements. One measurement will be made within 6 inches of the vessel bottom, one near the vessel center and one near the vessel top. Measurements are to be made at each location until the reading is stabilized. All hydrocarbons measured are to be assumed to be vinyl chloride.

(C) The production rate of polyvinyl chloride (Z) is to be determined by a method submitted to and approved by the Administrator.

(ii) A calculation based on the number of evacuations, the vacuum involved, and the volume of gas in the reactor is hereby approved by the Administrator as an alternative method for determining reactor opening loss for postpolymerization reactors in the manufacture of bulk resins.

STATUS OF COMPLIANCE

Compliance with 61.67(g)(5) is described under status of compliance for 61.64(a)(2).

§ 61.68 Emission Monitoring.

(a) A vinyl chloride monitoring system is to be used to monitor on a continuous basis the emissions from the sources for which emission limits are prescribed in Section 61.62(a) and (b), Section 61.63(a), and Section 61.64(a)(1), (b), (c), and (d), and for any control system to which reactor emissions are required to be ducted in Section 61.64(a)(2) or to which fugitive emissions are required to be ducted in Section 61.65 (b)(1)(ii), and (b)(2), (b)(5), (b)(6)(ii), and (b)(9)(ii).

(b) The vinyl chloride monitoring system(s) used to meet the requirement in paragraph (a) of this section is to be a device which obtains air samples from one or more points on a continuous sequential basis and analyzes the samples with gas chromotography or, if the owner or operator assumes that all hydrocarbons measured are vinyl chloride, with infrared spectrophotometry, flame ion detection, or an equivalent or alternative method. The vinyl chloride monitoring system used to meet the requirements in Section 61.65(b)(8)(i) may be used to meet the requirements of this section.

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61.68 Emission Monitoring(Continued)

(c) A daily span check is to be conducted for each vinyl chloride monitoring system used. For all of the emission sources listed in paragraph (a) of this section, except the one for which an emission limit is prescribed in Section 61.62(b), the daily span check is to be conducted with a concentration of vinyl chloride equal to 10 ppm. For the emission source for which an emission limit is prescribed in Section 61.62(b), the daily span check is to be conducted with a concentration of vinyl chloride which is determined to be equivalent to the emission limit for that source based on the emission test required by Section 61.67. The calibration is to be done with either:

(1) A calibration gas mixture prepared from the gases specified in sections 5.2.1 and 5.2.2 of Test Method 106 and in accordance with section 7.1 of Test Method 106, or

(2) A calibration gas cylinder standard containing the appropriate concentration of vinyl chloride. The gas composition of the calibration gas cylinder standard is to have been certified by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration does not change greater than ±5 percent from the certified value. The date of gas cylinder preparation, certified vinyl chloride concentration and recommended maximum shelf life must have been affixed to the cylinder before shipment from the manufacturer to the buyer. If a gas chromatograph is used as the vinyl chloride monitoring system, these gas mixtures may be directly used to prepare a chromatograph calibration curve as described in section 7.3 of Test Method 106. The requirements in sections 5.2.3.1 and 5.2.3.2 of Test Method 106 for certification of cylinder standards and for establishment and verification of calibration standards are to be followed.

STATUS OF COMPLIANCE

As explained in various sections of this plan, all vents are directed to the vapor recovery systems which compress and condense the VCM vapors. The VCM liquid is then recycled to polymerization. The noncondensible gases pass through these vapor recovery systems and collect in the vapor space of the recovered VCM receivers. These vapors are vented along with a small quantity of VCM vapor to the incinerator. The incinerator combustion gases are the only vapor vent to the atmosphere from vessels in VCM service. Emissions from the incinerator are monitored continuously by a gas chromotograph. Details on the maintenance and operating procedures are given in the approved Leak Detection and Elimination Plan. The plant follows the maintenance and operating procedure given in the Leak Detection and Elimination Plan.

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§ 61.69 Initial Report.

(a) An owner or operator of any source to which this subpart applies shall submit a statement in writing notifying the Administrator that the equipment and procedural specifications in Section 61.65 (b)(1), (b)(2), (b)(3), (b)(4), (b)(5), (b)(6), (b)(7), and (b)(8) are being implemented.

(b)(1) In the case of an existing source or a new source which has an initial startup date preceding the effective date, the statement is to be submitted within 90 days of the effective date, unless a waiver of compliance is granted under Section 61.11, along with the information required under Section 61.10. If a waiver of compliance is granted, the statement is to be submitted on a date scheduled by the Administrator.

(2) In the case of a new source which did not have an initial startup date preceding the effective date, the statement is to be submitted within 90 days of the initial startup date.

(c) The statement is to contain the following information:

(1) A list of the equipment installed for compliance,

(2) A description of the physical and functional characteristics of each piece of equipment,

(3) A description of the methods which have been incorporated into the standard operation procedures for measuring or calculating the emissions for which emission limits are prescribed in Section 61.65(b)(1)(i) and (b)(6)(i),

(4) A statement that each piece of equipment is installed and that each piece of equipment and each procedure is being used.

STATUS OF COMPLIANCE

The initial report and waiver of compliance application for the Aberdeen Chemical Plant was submitted December 20, 1976 and acknowledged by the EPA Region IV on December 29, 1976. Since that time, initial reports have been submitted on the following dates:

ITEM	DATE OF INITIAL REPORT
Batch Water Strippers	August 19, 1981
Reactor D-745	March 18, 1982
Reactor D-700	May 13, 1982
Increased Unloading Facilities	June 28, 1982
Spare Inert Vent Incinerator	July 13, 1982

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§ 61.70 Semiannual Report.

(a) The owner or operator of any source to which this subpart applies shall submit to the Administrator on September 15 and March 15 of each year a report in writing containing the information required by this section. The first semiannual report is to be submitted following the first full 6 month reporting period after the initial report is submitted.

(b)(1) In the case of an existing source or a new source which has been initial startup date preceding the effective date, the first report is to be submitted within 180 days of the effective date, unless a waiver of compliance is granted under Section 61.11. If a waiver of compliance is granted, the first report is to be submitted on a date scheduled by the Administrator.

(2) In the case of a new source which did not have an initial startup date preceding the effective date, the first report is to be submitted within 180 days of the initial startup date.

STATUS OF COMPLIANCE

The Aberdeen Chemical Plant submits semiannual reports as required by 61.70(a).

61.70 Semiannual Report.

(c) Unless otherwise specified, the owner or operator shall use the Test Methods in Appendix B to this part to conduct emission tests as required by paragraphs (c)(2) and (c)(3) of this section, unless an equivalent or an alternative method has been approved by the Administrator. If the Administrator finds reasonable grounds to dispute the results obtained by an equivalent or alternative method, he may require the use of a reference method. If the results of the reference and equivalent or alternative methods do not agree, the results obtained by the reference method prevail, and the Administrator may notify the owner or operator that approval of the method previously considered to be equivalent or alternative is withdrawn.

(1) The owner or operator shall include in the report a record of any emissions which averaged over any hour period (commencing on the hour) are in excess of the emission limits prescribed in Section 61.62(a) or (b), Section 61.63(a), or Section 61.64(a)(1), (b), (c), or (d), or for any control system to which reactor emissions are required to be ducted in Section 61.64(a)(2) or to which fugitive emissions are required to be ducted in Section 61.65 (b)(1)(ii), (b)(2),(b)(5),(b)(6)(ii), or (b)(9)(ii). The emissions are to be measured in accordance with Section 61.68.

STATUS OF COMPLIANCE

The incinerator is monitored continuously by a gas chromotograph as described in the status of compliance for section 61.68. Records of the measurements made by the gas chromotograph during monitoring are searched and any exceedances of 61.70(c)(1) are reported in the semiannual report.

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(2) In polyvinyl chloride plants for which a stripping operation is used to attain the emission level prescribed in Section 61.64(e), the owner or operator shall include in the report a record of the vinyl chloride content in the polyvinyl chloride resin. Test Method 107 is to be used to determine vinyl chloride content as follows:

STATUS OF COMPLIANCE

Section 61.70(c)(2) requires that Test Method 107 be used for the determination of the PVC slurry following steam stripping. Test Method 107 is written for Perkin-Elmer Corporation Head Space Analyzers model numbers F-40, F-42, and F-45. The manufacturing of these units and spare parts for some of these units has been discontinued by the Perkin-Elmer Corporation. New models of head space analyzers are being produced by both Perkin-Elmer and Hewlett Packard that are equivalent to the original instruments.

Vista is requesting that the EPA approve an equivalent test method for Method 107. This test method was developed by Vista and is referred to as "Test Method 107VA". This method is written as a performance specification instead of being specific to a particular model of head space analyzer. Also included in this equivalency request is a request to lengthen the maximum time allowed between sampling and analyses. This request is based upon test data developed by Vista demonstrating a method for holding samples for 5 days without loss of accuracy.

An item by item description of the differences between Test Method 107 and 107VA is given below and is then followed by a copy of Test Method 107VA.

Introduction - no modifications.

Paragraph 1.1 - Applicability and Principle - references to latex resin has been omitted.

Paragraph 1.2. - Principle - no modifications

Paragraph 2. - Range and Sensitivity - A performance specification for the instrument has been added to this section.

Paragraph 3. - The reference to corresponding operating parameters has been deleted. Operating parameters are equipment specific and have been deleted from Test Method 107VA. Please refer to revisions included under the paragraphs 8.3 through 8.3.5. for details.

Paragraph 4. - Precision and Reproducibility - no modifications.

Paragraph 5. - Safety - Safety procedures have been modified to specify the venting of vials in a laboratory hood to ensure that vinyl chloride is not vented into the laboratory atmosphere.

Paragraphs 6.1 through 6.1.3. - Apparatus, Sampling - no significant modifications.

Paragraphs 6.2 through 6.2.4. - Apparatus, Recovery - This section has been modified to include additional glass ware, septas, and other equipment, that are equivalent. In addition, the required accuracy of the analytical balance has been reduced. The decree of accuracy in weighing samples required by Method 107 does not affect the RVCM values. This modification will save considerable laboratory personnel time and will not affect the accuracy of the analyses.

Paragraphs 6.3 through 6.3.10. - Apparatus-Analyses - the entire section has been revised to be a performance specification rather than an equipment specification. Head space samplers, chromatographs, and chromatographic columns that have been found to be satisfactory are referenced. In addition to the three head space samplers mentioned in Test Method 107, Perkin-Elmer models HS-6, and HS-100 and Hewlett Packard model 19395A are listed as

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being satisfactory. The two Perkin-Elmer units are upgraded models of the units included in the standard and are acceptable units. Vista has conducted a study comparing the Hewlett Packard to the Perkin-Elmer F-42. The study demonstrates that it is an equivalent machine. Please refer to the attached report dated July 24, 1985. (Attachment C)

Paragraphs 7.1 through 7.2.1.2. - Reagents - Interference free hydrogen and nitrogen are used.

Paragraph 8.1.1 - PVC Sampling - No significant modifications.

Paragraph 8.1.2. - Water Sampling - The requirement to muffle the water sample vials has been deleted. The procedure serves no practical purpose. Sampling at Vista shows no interferences with unmuffled vials. Screw on caps are added provided tape is used to prevent the caps from loosening.

Paragraph 8.2. - Sample Recovery - Vista has developed a method of preserving samples for time periods of 5 days or longer. Vista data shows that refrigerated samples do not deteriorate if held for five days.

Attached is information previously submitted to the EPA requesting the 5 day holding period.(Attachment D) Listed below is data from the Vista Polymers Inc., Oklahoma City PVC plant showing that a 7 day hold period is also acceptable.

Vista Polymers Inc. Oklahoma City PVC Plant Data

The test was conducted between July 19, 1985 and July 26, 1985. On July 19, a two gallon slurry sample was taken from a reactor/slurry. Thirty sample vials and fifteen total solids samples were taken. Fifteen of the vials were analyzed on July 19 and the remaining fifteen vials were

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analyzed on July 26. As shown below, there is no statistically significant difference between the two sets of samples.

Samples Analyzed On July 19, 1985		Samples Analyzed On July 26, 1985	
Vial Number	RVCM(PPM)	Vial Number	RVCM(PPM)
1	74.5	2	73.5
3	82.5	4	75.1
5	76.9	6	73.3
7	77.4	8	68.2
9	68.0	10	69.1
11	75.0	12	65.8
13	63.1	14	88.2
15	69.4	16	54.5
17	72.4	18	61.6
19	68.1	20	70.3
21	64.8	22	63.0
23	67.7	24	70.0
25	69.2	26	72.2
27	63.5	28	63.8
29	66.7	30	57.2
Average	70.6		68.4
Standard Deviation	5.6		8.2

Paragraph 8.2.1. - Resin Samples - References to distilled water and dispersion resins have been deleted. As mentioned earlier, the accuracy of weight measurement has been revised.

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Paragraph 8.2.2. - Suspension Resin Slurry and Wet Cake - The accuracy of sample weight measurement has been revised and the reference to prepressurizing has been deleted. The prepressuring step is a function of operating conditions and equipment and is not required for our system.

Paragraph 8.2.3. - Dispersion Resin - Entire section has been deleted because of non-applicability.

Paragraph 8.2.4. - Inprocess Wastewater Samples - Sample weight measurement accuracy has been revised and references to prepressurization have been deleted.

Paragraphs 8.3.1. - through 8.3.4. - Analysis - Entire section has been revised to become a performance standard. Specific procedures pertain to only one model of equipment.

Paragraph 8.3.5. - Determination of TS - Procedure has been generalized to allow for flexibility in determing complete dryness.

Paragraphs 9.0 through 9.2 - Calibration - No significant modifications.

Paragraphs 10.1 through 10.2 - Calculations - No significant modifications.

Test Method 107VA is given below:

METHOD 107VA

Determination of Vinyl Chloride Content of Inprocess Wastewater Samples and Vinyl Chloride Content of Polyvinyl Chloride Resin, Slurry, and Wet Cake samples.

Introduction

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph (GC) nor by those who are unfamiliar with source sampling because knowledge beyond the scope of this presentation is required. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen.

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1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of the vinyl chloride monomer (VCM) content of inprocess wastewater samples and the residual vinyl chloride monomer (RVCM) content of polyvinyl chloride (PVC) resins, wet cake, and slurry samples. It cannot be used for polymer in fused forms such as sheet or cubes.

1.2 Principle. The basis for this method relates to the vapor equilibrium that is established between RVCM, PVC resin, water, and air in a closed system. The RVCM in a PVC resin will equilibrate rapidly in a closed vessel, provided that the temperature of the PVC resin is maintained above the glass transition temperature of that specific resin.

2. Range and Sensitivity. The lower limit of detection of vinyl chloride will vary according to the sampling and chromatographic system. The system must be capable of precisely measuring the VCM peak in a 50-VPPM gas mixture standard using the same conditions as used for sample analyses and the measured peak must be at least 10 times the background noise level. With proper calibration, the upper limit may be extended as needed.

3. Interferences. The chromatograph columns herein described normally provide an adequate resolution of vinyl chloride; however, resolution interferences may be encountered on some sources. Therefore, the chromatograph operator shall select the column and operating parameters best suited to his particular analysis requirements, subject to the approval of the Administrator. Approval is automatic provided that the tester produces confirming data through an adequate supplemental analytical technique such as analysis with a different column or GC/mass spectroscopy and has the data available for review by the Administrator.

4. Precision and Reproducibility. An interlaboratory comparison between

seven laboratories of three resin samples, each split into three parts, yielded a standard deviation of 2.63 percent for a sample with a mean of 2.09 ppm, 4.16 percent for a sample with a mean of 1.66 ppm, and 5.29 percent for a sample with a mean of 62.66 ppm.

5. Safety. Do not release vinyl chloride to the laboratory atmosphere during preparation of standards. Venting or purging with VCM/air mixtures must be held to a minimum. When they are required, the vapor must be routed to outside air. Vinyl chloride, even at low ppm levels, must not be vented inside the laboratory. After vials have been analyzed, the gas contained in the vial must be vented in a laboratory hood that is routed to outside air.

6. Apparatus.

6.1. Sampling. The following equipment is required:

6.1.1. Glass bottles. 60-ml (2-oz.) capacity with wax-lined screw-on tops for PVC samples.

6.1.2. Glass Vials. 20-50-microliter capacity Hypovial, sealed with Teflon faced Tuf-Bond discs for water samples.

6.1.3. Adhesive Tape. To prevent loosening of bottle tops.

6.2. Sample Recovery. The following equipment is required:

6.2.1. Glass Vials. 22 ml capacity with butyl rubber septa, Perkin-Elmer Corporation Nos. 0105-0129 (glass vials), B001-0728 (gray butyl rubber septum, plug style), 0105-0131 (butyl rubber septa), Shamrock Glass Co. Nos. 778701 (glass vials), 778709 (gray butyl rubber septum), have been found to be acceptable. The seals must be made from butyl rubber. Silicone rubber seals are not acceptable.

6.2.2. Analytical Balance. Capable of weighing to ±0.001 grams.

6.2.3. Vial Sealer. Perkin-Elmer No. 105-0106, Pierce Chemical Co. No. 13212, or equivalent.

6.2.4. Syringe. 100-microliter capacity, precision series "A" No. 010025, or equivalent.

6.3 Analysis. The following equipment is required:

6.3.1. Headspace Sampler. Must be capable of injecting a constant amount of headspace gas from a vial maintained at 90.0± 0.5°C. Perkin-Elmer Corporation Model F-40, F-42, F-45, HS-6, or HS-100 Head-Space Analyzer; and Hewlett-Packard model 1939A Head-Space Analyzer have been found to be satisfactory.

6.3.2. Gas Chromatograph and Columns. Chromatograph to be equipped with flame ionization detection system and backflush capabilities. Chromatographic columns must elute VCM in a sharp, symmetrical peak within a short time (0.7 to 3 minutes) with adequate resolution from other components found in the samples. (Adequate resolution is defined as an area overlap of not more than 10 percent of the vinyl chloride peak by an interferent peak. Calculation of area overlap is explained in Appendix C, Procedure 1: "Determination of Adequate Chromatographic Peak Resolution".) Columns of a nominal 2 m X 1/8 inch O.D. containing chromasorb 101, Porapak Q, and Carbowax 1500 on either Carbopak B or Carbopak C have been found to be satisfactory.

6.3.3. Thermometer. 0 to 100° C., accurate to ± 0.1°C.

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6.3.4. Integrator-Recorder.

6.3.5. Regulators. For required gas cylinders.

6.3.6. Barometer, Accurate to 1 mm Hg.

7. Reagents. Use only reagents that are of chromatographic grade.

7.1. Analysis. The following items are required for analysis:

7.1.1. Hydrogen. Interference free.

7.1.2. Nitrogen. Interference free.

7.1.3. Air. Zero grade.

7.1.4. Water. Interference free.

7.2. Calibration. The following items are required for calibration:

7.2.1. Cylinder Standards(5). Gas mixture standards (approximately 50, 500, 2000, and 4000 ppm vinyl chloride in nitrogen cylinders). The tester may use cylinder standards to directly prepare a chromatograph calibration curve as described in Section 9.2. if the following conditions are met: (a) The manufacturer certifies the gas composition with an accuracy of ± 3 percent or better (b) The manufacturer recommends a maximum shelf life over which the gas concentration does not change by greater than ± 5 percent from the certified value, (c) The manufacturer affixes the date of gas cylinder preparation, certified vinyl chloride concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

7.2.2.1. Cylinder Standards Certification. The manufacturer shall certify the concentration of vinyl chloride in nitrogen in each cylinder by (a) directly analyzing each cylinder and (b) calibrating his analytical procedure on the day of

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cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a 3-point calibration curve. It is recommended that the manufacturer maintain (1) a high concentration calibration standard (between 4000 and 8000 ppm) to prepare his calibration curve by an appropriate dilution technique and (2) a low concentration calibration (between 50 and 500 ppm) to verify the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low-concentration calibration standard exceeds 5 percent of the true concentration, the manufacturer shall determine the source of error and correct it, then repeat the 3-point calibration.

7.2.1.2. Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify each calibration standard by (a) comparing it to gas mixtures prepared (with 99 mole percent vinyl chloride) in accordance with the procedure described in Section 7.1 of Method 106 or by (b) calibrating it against vinyl chloride cylinder Standard Reference Materials (SRM's) prepared by the National Bureau of Standards if such SRM's are available. The agreement between the initially determined concentration value and the verification concentration value must be within + 5 percent. The manufacturer must reverify all calibration standards on a time interval consistent with the shelf life of the cylinder standard sold.

8. Procedure.

8.1. Sampling.

8.1.1. PVC Sampling. Allow the resin or slurry to flow from a tap on the tank or line until the tap line has been well purged. Extend and fill a 60 ml. sample bottle under the tap and immediately tighten a cap on the bottle. Wrap adhesive tape around the cap and bottle to prevent the cap from loosening. Place an identifying label on each bottle, and record the date, time, and sample location both on the bottles and in a log book.

8.1.2. Water Sampling. At the sampling location fill the vials bubble-free to overflowing so that a convex meniscus forms at the top. The excess water is displaced as the sealing disc is carefully placed, with the Teflon side down, on the opening of the vial.

Place the aluminum seal over the disc and the neck of the vial, and crimp into place. Affix an identifying label on the bottle, and record the date, time, and sample location both on the vials and in a log book. All samples must be kept refrigerated until analyzed. (Screw on caps can be used in place of aluminum caps if adhesive tape is used to prevent the cap from loosening.)

8.2. Sampling Recovery. Sample analyses must be completed within 5 days. Samples held over 24 hours must be refrigerated.

8.2.1. Resin Samples. The weight of the resin used must be between

2.0 and 5.0 grams. Add 100 micro-liters or about two equal drops of water, to the dry sample and immediately seal the vial. Report the sample weight on the data sheet; it is required for calculation of RVCM. An exact weight must be obtained (± 0.01 g) for each sample. Condition them for a minimum of 1 hour in the 90°C bath. Do not exceed 5 hours.

NOTE: Some aluminum vial caps have a center section that must be removed so the injection needle will not be damaged.

8.2.2. Suspension Resin Slurry and Wet Cake Samples. Decant the water from a slurry sample, and turn the sample bottle on its side on a paper towel. Wait for the water to drain, place approximately 0.2 to 4.0 grams of the wet cake sample in a tared vial (tared, including septum and aluminum cap) and seal immediately. Then determine the sample weight (±0.01 g). All samples must be conditioned for 1 hour at 90°C. A sample of wet cake is used to determine total solids (TS). This is required for calculating RVCM.

8.2.3. Inprocess Wastewater Samples. Using a tared vial (tared, including septum and aluminum cap) quickly add approximately 1 cc of water using a medicine dropper. Seal the vial as soon as possible. Determine sample weight (±0.01 g). Condition for 1 to 2 hours as required at 90°C in the analyzer bath.

8.3 Analysis.

8.3.1. Preparation of Equipment.

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8.3.1.1. Preparation of the Chromatograph. Chromatographic column must be conditioned prior to the first use. The carrier gas flow should be adjusted according to the column being used (20 - 30 cc/min for 1/8 inch O.D. is typical), and balanced with the backflush system according to the manufacturer's directions. Hydrogen and air flow to the detector should be adjusted for the carrier flow according to the manufacturer's directions.

8.3.1.2. Temperature adjustments. Set temperatures as follows:

a. Chromatographic Column Oven. Establish temperature necessary to elute VCM from the column as a sharp resolved peak per Section 6.3.2.

b. Chromatograph Injector. 100 to 150°C.

c. Chromatograph Detector. 100°C or 25° above column oven, whichever is greater.

d. Sample Equilibration Chamber. 90 ± 1°C.

8.3.1.3. Integrator Settings. Optimize integration parameters according to the manufacturer's directions for the particular VCM peak shape obtained by your chromatograph.

8.3.1.4. Headspace Sampler Program. Establish sampling conditions according to the manufacturer's directions to provide a reproducible sample injection of sufficient volume to give the required sensitivity for the 50-VPPM gas mixture standard.

8.3.1.5. Backflush Valve. Determine time to activate backflush valve after elution of the VCM peak for your chromatographic conditions.

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8.3.1.6. Determine the amplifier range setting for your system to provide a linear response for all four calibration gas standards (50 to 4000 VPPM).

8.3.2. Preparation of Sample Turntable. Insert samples in the following order:

Position 1 and 2 - Old 2000 ppm standards for conditioning. These are necessary only after the analyzer has not been used for 24 hours or longer.

Position 3 - 50 ppm standard, freshly prepared.

Position 4 - 500 ppm standard, freshly prepared.

Position 5 - 2000 ppm standard, freshly prepared.

Position 6 - 4000 ppm standard, freshly prepared.

Position 7 - Sample No. 8 (This is the first sample of the day, but is given as 8 to be consistent with the turntable and the integrator printout.)

After samples have been positioned, insert the second set of 50, 500, 2000, and 4000 ppm standards. Samples including standards, must be conditioned in the bath of 90° C for 1 hour (not to exceed 5 hours).

8.3.3. Record ambient laboratory temperature and pressure.

8.3.4. Start Chromatograph Program. When all samples, including standards, have been conditioned at 90°C for 1 hour, start the analysis program according to the manufacturer's instructions. These instructions must be carefully followed when starting and stopping a program to prevent damage to the injection assembly.

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8.3.5. Determination of TS. For wet cake and slurry, determine TS for each sample by accurately weighing approximately 3 to 4 grams of sample in an aluminum pan before and after placing in a draft oven (105 to 110°C). Samples must be dried to constant weight. The TS are then calculated as the final sample weight divided by initial sample weight.

9. Calibration Calibration is to be performed each 24 hour period when the instrument is used. Each day the analyzer has not been used in more than 24 hours as specified in 8.3.2., prior to running the samples, the column should be conditioned by running two 2000 ppm standard from the previous day.

9.1. Preparation of Standards. Calibration standards are prepared as follows: Place about two equal drops of water into sample vial before filling or inject 100 microliters water after sealing vial. Then fill the vial with the VCM/nitrogen standard, rapidly seat the septum, and seal with the aluminum cap. Use a 1/8 inch stainless steel line from the cylinder to the vial. Do not use rubber or tygon tubing. The sample line from the cylinder must be purged (into a properly vented hood) prior to filling the vials. After purging, reduce the flow rate to 500 to 1000 cc/min. Place end of tubing into vial (near bottom). Position a septum on top of the vial, pressing it against the 1/8" filling tube to minimize the size of the vent opening. This is necessary to minimize mixing air with the standard in the vial. Each vial is to be purged with standard for 10 vial volumes during which time the filling tube is gradually slid to the top of the vial.

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The tube is removed with the septum, simultaneously sealing the vial. Practice will be necessary to develop good technique. Rubber gloves should be worn during the above operations.

9.2. Preparation of Chromatograph Calibration Curve.

Prepare two 50, 500, 2000, and 4000 ppm standard samples. Run the calibration samples in exactly the same manner as regular samples. Plot A_s, the integrator area counts for each standard sample, versus C_c the concentration of vinyl chloride in each standard sample. Draw a straight line through the points derived by the least squares method.

10. Calculation.

10.1. Response Factor. If the calibration curve described in Section 9.2 passes through zero, a response factor, R_f may be used to compute vinyl chloride concentrations. To compute a response factor, divide any particular A_s by the corresponding C_c.

$$R_f = \frac{A_s}{C_c} \qquad \text{Eq. 107-1}$$

10.2. Residual Vinyl Chloride Monomer Concentration, (C_{rvc}) or Vinyl Chloride Monomer Concentration. Calculate C_{rvc} in ppm or mg/kg as follows:

$$C_{rvc} = \frac{A_s P_a}{R_f T_1}\left[\frac{M_v V_g}{R m} + K_p (TS) T_2 + K_w (1-TS) T_2\right] \text{EQ. 107-2}$$

Results calculated using these equations represent concentrations based on the total sample. To obtain results based on dry PVC content, divide by TS.

61.70 Semiannual Report (Continued)

Where:

A_s = Chromatograph area counts of vinyl chloride for the sample.

P_a = Ambient atmospheric pressure, mm Hg.

R_f = Response factor in area counts per ppm VCM.

T_1 = Ambient laboratory temperature, °K.

M_v = Molecular weight of VCM 62.5 g/mole.

V_g = Volume of the vapor phase, cm^3.

R^g = Gas constant (62360 cm^3) (mm Hg/mole) (°K).

m = Sample weight, g.

K_p = Henry's Law Constant for VCM in PVC@90°C, 6.52 X 10^{-6} g/g/mm Hg.

TS = Total solids expressed as a decimal fraction.

T_2 = Equilibrium temperature, °K.

K_w = Henry's Law Constant for VCM in water @ 90°C, 7 X 10^{-7} g/g/mm Hg.

Assuming the following conditions are met, these values can be substituted into Equation 107-2.

P_a = 750 mm Hg.

V_g = Vial volume - sample volume (Fisher vials are 22.0 cm^3 and Perkin-Elmer Vials are 21.8 cm^3) = Vial Volume - $\frac{m(TS)}{1.36} - \frac{m(1-TS)}{0.9653}$

T_1 = 296°K.

T_2 = 363°K.

$$C_{rvc} = \frac{A_{s750}}{R_f 296}\left[\frac{62.5\left(21.8 - \frac{m(TS)}{1.36} - \frac{m(1-TS)}{0.9653}\right)}{62360\ m} + 6.25\times10^{-6}(TS)(363) + 7.0\times10^{-7}(1-TS)(363)\right]$$

If the calibration curve does not pass through zero, the calibration curve must be employed to calculate each sample concentration unless the error introduced by using a particular R_f is known.

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61.70 Semiannual Report.

(i) If batch stripping is used, one representative sample of polyvinyl chloride resin is to be taken from each batch of each grade of resin immediately following the completion of the stripping operation, and identified by resin type and grade and the date and time the batch is completed. The corresponding quantity of material processed in each stripper batch is to be recorded and identified by resin type and grade and the date and time the batch is completed.

STATUS OF COMPLIANCE

Compliance with 61.70(c)(2)(i) is described under status of compliance for section 61.64(e)(1)(ii).

(ii) If continuous stripping is used, one representative sample of polyvinyl chloride resin is to be taken for each grade of resin processed or at intervals of 8 hours for each grade of resin which is being processed, whichever is more frequent. The sample is to be taken as the resin flows out of the stripper and identified by resin type and grade and the date and time the sample was taken. The corresponding quantity of material processed by each stripper over the time period represented by the sample during the 8 hour period, is to be recorded and identified by resin type and grade and the date and time it represents.

STATUS OF COMPLIANCE

Continuous stripping is not used at the Aberdeen Chemical Plant. This section is not applicable.

61.70 Semiannual Report.

(iii) The quantity of material processed by the stripper is to be determined on a dry solids basis and by a method submitted to and approved by the Administrator.

STATUS OF COMPLIANCE

Compliance with 61.70(c)(2)(iii) is described under status of compliance for section 61.64(e)(1)(ii).

(iv) At the prior request of the Administrator, the owner or operator shall provide duplicates of the samples required in paragraphs (c)(2)(1) and (c)(2)(ii) of this section.

STATUS OF COMPLIANCE

Upon request, the Aberdeen Chemical Plant will provide duplicate samples to the Administrator as required in 61.70(c)(2)(i) and 61.70(c)(2)(ii).

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61.70 Semiannual Report (Continued)

(v) The report to the Administrator by the owner or operator is to include the vinyl chloride content found in each sample required by paragraphs (c)(2)(i) and (c)(2)(ii) of this section, averaged separately for each type of resin, over each calendar day and weighted according to the quantity of each grade of resin processed by the stripper(s) that calendar day, according to the following equation:

$$AT_i = \frac{\sum_{i=1}^{n} P_{Gi} M_{Gi}}{Q_{Ti}} = \frac{P_{Gi} M_{Gi} + P_{G2} M_{G2} + \ldots + P_{Gn} M_{Gn}}{Q_{Ti}}$$

Where:

A = 24-hour average concentration of type T_i resin in ppm (dry weight basis).

Q = Total production of type Ti resin over the 24-hour period, in kg.

T_i = Type of resin; i=1,2...m where m is total number of resin types produced during the 24-hour period.

M = Concentration of vinyl chloride in one sample of grade Gi resin, in ppm.

P = Production of grade G_i resin represented by the sample, in kg.

G_i = Grade of resin; e.g., G_1, G_2, and G_3.

n = Total number of grades of resin produced during the 24-hour period.

STATUS OF COMPLIANCE

Compliance with 61.70(c)(2)(v) is described under section 61.64(e).

(vi) The owner or operator shall retain at the source and make available for inspection by the Administrator for a minimum of 2 years records of all data needed to furnish the information required by paragraph (c)(2)(v) of this section: The records are to contain the following information:

(A) The vinyl chloride content found in all samples required in paragraphs (c)(2)(i) and (c)(2)(ii) of this section, identified by the resin type and grade and the time and date of the sample, and

(B) The corresponding quantity of polyvinyl chloride resin processed by the stripper(s), identified by the resin type and grade and the time and date it represents.

STATUS OF COMPLIANCE

Records of the vinyl chloride content of the slurry stripped in the reactors and corresponding production for the batch are maintained at the plant for a minimum of two years.

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61.70 Semiannual Report(Continued)

(3) The owner or operator shall include in the report a record of the emissions from each reactor opening for which an emission limit is prescribed in Section 61.64(a)(2). Emissions are to be determined in accordance with Section 61.67(g)(5), except that emissions for each reactor are to be determined. For a reactor that is also used as a stripper, the determination may be made immediately following the stripping operation.

STATUS OF COMPLIANCE

Compliance with 61.70(c)(3) is described under status of compliance for section 61.64(a)(2).

§ 61.71 Recordkeeping.

(a) The owner or operator of any source to which this subpart applies shall retain the following information at the source and make it available for inspection by the Administrator for a minimum of two years;

(1) A record of the leaks detected by the vinyl chloride monitoring system, as required by Section 61.65(b)(8), including the concentrations of vinyl chloride measured, analyzed, and recorded by the vinyl chloride detector, the location of each measurement and the date and approximate time of each measurement.

(2) A record of the leaks detected during routine monitoring with the portable hydrocarbon detector and the action taken to repair the leaks, as required by Section 61.65(b)(8), including a brief statement explaining the location and cause of each leak detected with the portable hydrocarbon detector, the date and time of the leak, and any action taken to eliminate that leak.

(3) A record of emissions measured in accordance with Section 61.68.

(4) A daily operating record for each polyvinyl chloride reactor, including pressures and temperatures.

STATUS OF COMPLIANCE

Records prescribed by §61.71 are retained at the Plant and are available for inspection by the Administrator.

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61.70 Recordkeeping(Continued)

Specific Training

Aberdeen will prepare and maintain a document containing updated procedures for which training will be done as specified under Sections 61.64(a)(2), 61.65(a), 61.65(b)(1)(i)&(ii), 61.65(b)(5), 61.65(b)(6)(i)&(ii), 61.65(b)(7), 61.65(b)(8) and 61.65(b)(9)(i) of this Plan. This retraining will be a minimum of four hours per year. Updating and initital retraining as required by this Plan will be completed within 270 days of Plan approval.

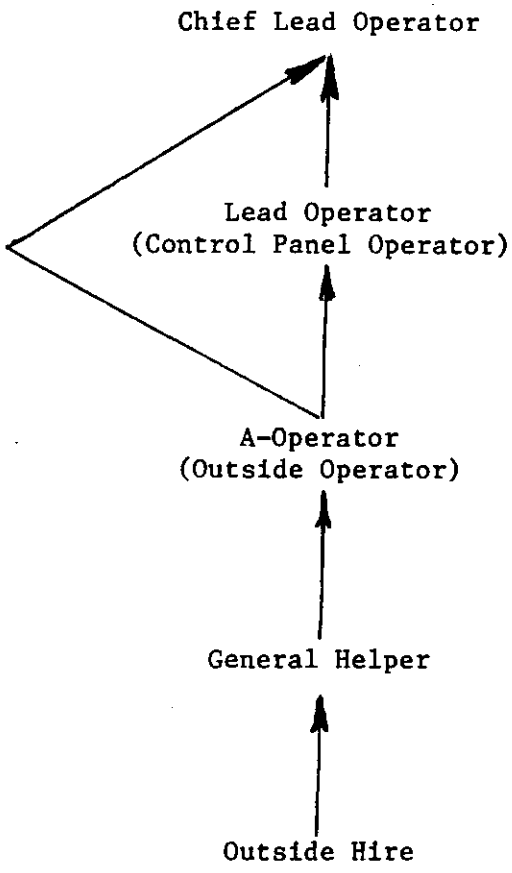
General Training

The Aberdeen Chemical Plant will continue with the general training program in the Vinyl unit which ensures trained personnel operating equipment. A description of this training program is listed below.

A new hire enters the plant in the General Helper classification. In this classification the employee may work in any of the production areas depending on overall manpower requirements. The Aberdeen plant consists of four major production areas which are polyvinyl chloride, dry blend, compound and plasticizer. The NESHAP for vinyl chloride covers only the operation of the polyvinyl chloride production area.

General Training (Continued)

Normal progression in the polyvinyl chloride production area is illustrated below:



A General Helper working in the polyvinyl chloride production area does not perform operator functions until he starts his training to become an A-Operator. Prior to starting the training program the General Helper does such tasks as bagging PVC resin, cleaning dryers, changing dust collector socks, pumping pond resin and being a fire watch.

The current training program in the polyvinyl chloride area consists of on-the-job training, training by supervision and testing. Often operators are trained such that they are qualified to perform the duties of the next

General Training (Continued)

higher position. This is done to assure qualified personnel are available to provide coverage for vacations, sickness, National Guard Duty etc. When an employee is selected to train up, the first step is an orientation introduction conducted by the Operations Supervisor and the Shift Supervisor. In this session the functions of the position are discussed and the importance of knowing the unit and understanding the process is stressed. Safety and environmental responsibilities are also covered in this first meeting. The trainee then starts on-the-job training with a qualified operator. The trainee works alongside the qualified operator to observe and learn the routine duties and responsibilities required to satisfactorily perform the job. The on-the-job training is conducted for approximately 300 hours. During the on-the-job training period the progress of the trainee is monitored by the Chief Lead Operator and the Shift Supervisor. Also during the on-the-job training period the trainee is given a list of questions which he studies and must answer verbally and in writing to successfully complete the training. The employee must also demonstrate to the Shift Supervisor that he/she has learned all the duties of the new position. This is accomplished with the use of check lists. Upon approval by the Shift Supervisor and the Operations Supervisor the employee is then officially deemed to be qualified for the job and at the time is then allowed to perform the job on his/her own.

In case there is an open position which needs to be filled and the person selected is not completely trained, the training program described above is used to qualify the person for the new position. The normal progression of

General Training (Continued)

a General Helper is to A-Operator to either the Lead Operator or to Chief Lead Operator. The Lead Operator can also progress to the Chief Lead Operator.

The Shift Supervisors observe and train the personnel on their shifts on a continuing basis. The normal make up of a shift includes the Shift Supervisor,Chief Lead Operator, Lead Operators and A-Operators. Since the number of operators on a shift is quite small, the Shift Supervisor per sonally checks their performance and corrects any problems if they should occur.

Several possibilities exist during the training program. If the operator in training decides for some reason he does not want to continue the training for the next level, he can return to his previous position. If after the 300 hours of on-the-job training the Shift Supervisor and the Operations Supervisor consider the employee does not have the ability to master the new position, the employee returns to his/her previous position. If the Shift Supervisor and the Operations Supervisor consider the trainee is making progress and learning the new position but is not fully capable to handle the new job after the 300 hours of on-the-job training, more on-the-job training is continued until the person is fully trained to do the new position on his/her own.

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ATTACHMENT A

RUPTURE DISC/RELIEF VALVE

PRACTICES MANUAL

VISTA POLYMERS INC.

ABERDEEN, MS

UPDATED SEPTEMBER 16, 1985

RUPTURE DISC/RELIEF VALVE

PRACTICES MANUAL

TABLE OF CONTENTS

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I. INTRODUCTION

Section 61.65 (b)(4) of the National Emission Standards for Hazardous Air Pollutants requires that a rupture disc be installed underneath any relief valve in vinyl chloride service minimize leakage through the relief valve to the atmosphere. In accordance with this requirement, Vista Polymers Inc. has installed a large number of rupture discs in vinyl chloride service throughout the plant. In addition to preventing relief valve leakage, rupture discs also serve the vital function of protecting the relief valve from polymer buildup on the relief valve seat, which could hinder the proper functioning of the relief valve in an emergency. In either case, proper functioning of the rupture disc/relief valve combination is essential for plant safety.

This program has been developed because of the importance of maintaining the integrity of rupture discs during their handling and installation. Adherence to the procedures outlined in this manual will help to ensure that the chance of rupture disc/relief valve malfunctions will be minimized, and that thorough documentation will be available whenever such a malfunction does occur. This documentation may become extremely critical in the event of a VCM release caused by a premature rupture disc failure or other process upset conditions.

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II. RUPTURE DISC ORDERING AND PRE-INSTALLATION CHECKOUT

A. Specification of Rupture Discs

All rupture discs in VCM service are listed on Table 1. The following specifications should be noted on the purchase order when ordering these rupture discs.

1. Disc size (specify).
2. Type S-90.
3. Nickel material.
4. 0% Manufacturing range.
5. Burst pressure (specify).
6. Burst temperature.
7. Certification of performance.
8. ASME code stamped and certified.
9. Test each disc to 90% of rated burst pressure.
10. Replaces lot no. . . . (specify).
11. Serially number all discs in the lot.

B. Lot Inspection and Pre-Testing

All new rupture disc lots received at the plant receiving dock must be thoroughly inspected and tested before they are moved to the storeroom. The following procedures are to be used when new rupture disc lots are received at the Plant:

1. When a lot of rupture discs arrives at the receiving dock, care must be exercised when unloading the discs from the truck so as not to damage the discs.

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II. RUPTURE DISC ORDERING AND PRE-INSTALLATION CHECKOUT - Continued

B. Lot Inspection and Pre-Testing - continued

2. The receiver must notify Processing Engineering that there are new rupture discs at receiving, and a Process Engineer or other trained personnel will count the number of discs in the lot and inspect each individual disc for flaws.

3. A flaw in a disc is defined as follows:

   a. Any scratch or indentation which can be felt on the opposite side of the disc.

   b. Any irregularity in the shape of the domed portion of the disc that can be seen with the eye or felt.

   c. A pinhole or scratch which could cause the disc to leak.

   d. A disc without a tag.

   e. A disc that will not fit the pins of a holder.

   f. A disc that is labeled differently than the other discs in the same lot.

4. Flawed discs must be removed from the lot and returned to the manufacturer. Discs which pass inspection are initialed on the box by the inspector.

5. Rupture discs which are to be installed on vessels in VCM service must be approved by lot before they can be placed in the storeroom. One disc from each of these lots will be sent to the maintenance shop and burst using the procedures specified in the destructive testing section of this manual.

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II. RUPTURE DISC ORDERING AND PRE-INSTALLATION CHECKOUT - Continued

B. Lot Inspection and Pre-Testing - continued

6. If any rupture disc does not burst within 5% of its rated burst pressure, the entire lot from which the disc was taken must be returned to the manufacturer. Maintenance must notify receiving that these discs have either passed or failed this test.

7. Rupture discs which pass inspection and testing are ok'd for placement in the storeroom. Rupture disc boxes which have not been initialed are not to be placed in the storeroom.

C. Recordkeeping

Administrative Services must keep a record of rupture disc receiving and inspection data. An example logsheet is attached. This information must be stored in the plant for a period of at least two years.

III. RUPTURE DISC INSTALLATION

A qualified maintenance installation observer must be present during all phases of rupture disc installation (vinyl reactors only). The Mechanical Superintendent will keep an updated list of qualified maintenance installation observers.

A. Installation in Holders

All rupture discs must be installed in the holders according to the manufacturer's specifications. These written specifications come with each rupture disc. The following steps outline the general procedure which is to be used when installing rupture discs in holders:

III. RUPTURE DISC INSTALLATION (Continued)

A. Installation in Holders - continued

1. Before a disc is placed in the holder, the disc, the holder and the holder bolts must be inspected for flaws.

2. Flaws are defined as follows:

   a. A disc that has any of the defects listed in Section II (B)(3).

   b. A holder face that is covered with dirt or debris, or is deeply gouged such that it will leak when installed.

   c. Set screws that are galled or cannot be screwed into the holder by hand.

   d. A holder with a damaged bite ring. A holder is considered damaged if there are indentations or flat spots on the bite ring. This is determined from a visual inspection of the holder. Also, the height of the bite ring must be checked. This is done by the inspector running his fingernail around the bite ring. The bite ring has sufficient height to be reused if it holds the fingernail all the way around the circumference of the bite ring.

3. Flaw components must not be installed in the Plant.

4. Place the disc in the holder and hand install the holder bolts. Using a torque wrench, tighten the holder bolts to the torque specified by the manufacturer. This tightening must be performed in at least four passes; i.e. 25%, 50%, 75% and 100% of the final torque. A criss-cross tightening pattern must be used when torquing the bolts.

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III. RUPTURE DISC INSTALLATION - Continued

A. Installation in Holders - continued

5. When the installation of the disc in the holder is complete, visually inspect the disc again to see if it has been distorted or otherwise damaged.

6. Rupture discs must not be removed from the holders after installation, otherwise the rupture disc must be discarded.

B. Pressure Testing in the Shop

All reactor rupture discs are to be pressure tested in the maintenance shop to 90% of their rated burst pressure before being installed in the plant. The following testing procedure must be used when pressure testing rupture discs in the maintenance shop.

1. Clean the flanges of the test bench and the faces of the rupture disc holder where the two surfaces meet. Use an asbestos gasket between the flange and the holder.

2. Install the holder on the test bench and tighten the bolts in a criss-cross pattern, making several passes on each bolt.

3. Warn nearby personnel that a rupture disc is being pressure tested.

4. Using pressurized air, slowly open the test valve and pressurize the space underneath the rupture disc. Increase the pressure to 90% of the rupture disc burst pressure at $72^{o}F$.

5. Slowly depressurize the space underneath the rupture disc and remove the assembly from the test bench. If the disc appears to have been distorted or otherwise damaged during the test, do not install the disc in the plant.

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III. RUPTURE DISC INSTALLATION - Continued

B. Pressure Testing in the Shop - continued

6. If a rupture disc bursts prematurely (less than 90% of its rated burst pressure) or is damaged by the test, the disc must be given intact to Process Engineering.

7. The calibration of the test bench pressure gauge will be checked with a dead weight pressure gauge every six months.

C. Installation In The Plant

Rupture disc assemblies must be installed in the plant accordingly:

1. Before installing the holder assembly between the companion flanges, thoroughly clean the flange faces with a putty knife to remove any solid buildup or debris.

2. Check to see that the flange faces are not gouged or otherwise damaged. Place the rupture disc between the flanges, with the bulged-out side of the disc facing the process.

3. On reactors, use asbestos-type gaskets only. Flexatalik gaskets may be used elsewhere in the plant if desired.

4. When tightening the companion flanges, torque the bolts to the manufacturer's specification using a criss-cross tightening pattern. Make at least four passes on each bolt.

D. Pressure Checking After Installation on the Reactor

After a rupture disc has been installed on a reactor, the reactor will be pressure checked before it is charged. The reactors will be pressure checked to 90% of the pressure of the lowest rated rupture disc on the reactor or 170 $\#/in^2$, whichever pressure is lower.

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III. RUPTURE DISC INSTALLATION - Continued

D. Pressure Checking After Installation on the Reactor - continued

The pressure check must be witnessed by an approved pressure check observer. A list of approved pressure check observers is kept on the Vinyl Shift Supervisor's bulletin board.

The pressure checking consists of filling the reactor with water and then increasing the pressure in the reactor to the desired pressure per established procedures. The operators involved must be extremely careful during pressure check procedures not to burst or damage a rupture disc. Bursting a disc during the pressure check will cause reactor downtime to change the disc. A disc can be damaged by hydraulic shock if the reactor becomes liquid full during the pressure check. A damaged rupture disc may burst at lower than the rated pressure, causing leakage through the reactor relief valve. In addition, a damaged disc may not burst at the rated pressure, which could allow a reactor to overpressure. The pressure check observer must witness the pressure check from the field and must verify the final reactor pressure. The reason for the pressure check, the signature of the approved observer, the final reactor pressure, and other test findings will be noted in the reactor pressure check log kept in the Vinyl control room.

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IV. RUPTURE DISC REMOVAL

A. Rupture Disc Changeout

Rupture discs are to be removed from service and changed accordingly:

1. Any rupture disc which fails in service must be changed as soon as possible after it is discovered that the disc has failed.
2. Any rupture disc which is believed to be covered with resin or otherwise damaged must be changed as soon as possible.
3. All rupture discs on reactors will be changed at least once every twelve months.
4. When a reactor is taken out of service for condenser drilling, the condenser rupture disc(s) will be removed or guard(s) will be installed over the rupture disc nozzle(s) before the drilling operation is started.
5. Any rupture disc which fails in reactor service must be given to Process Engineering.

B. Destructive Testing

All rupture discs taken off of vinyl reactors must be burst in the maintenance shop when taken out of service permanently. The following procedures also apply to new rupture discs which are to be burst when they arrive at the Plant.

1. When removing the holder assembly from the reactor and when transporting the holder assembly to the maintenance shop, use caution so as not to damage the disc or the holder.

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IV. RUPTURE DISC REMOVAL - Continued

B. Destructive Testing - continued

2. When destructively testing a vinyl reactor rupture disc, a qualified maintenance installation observer must be present to observe the testing.

3. Install the holder assembly on the test bench and pressurize the disc with air until the disc bursts.

4. If a rupture disc bursts prematurely (less than 90% of its rated burst pressure), the disc must be given to Process Engineering. Use care so as not to damage these discs.

V. RECORDKEEPING

A record must be kept of all rupture disc installation and testing data. An example logsheet is attached. This information must be stored in the plant for a period of at least two years.

VI. TRAINING

All maintenance and engineering personnel involved in this program are to receive hands-on training in the installation and handling of rupture discs once each calendar year. Records of all personnel who attend these training sessions are to be kept for a period of at least two years.

VII. RELIEF VALVES

All relief valves in vinyl chloride service will be periodically checked to assure that they will operate properly in an emergency situation.

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VII. RELIEF VALVES - Continued

A. Reactor Relief Valves

The past practice of testing the relieving pressure of reactor relief valves in place can no longer be used due to the change in the setting of the blowdown ring. With the new settings, the quantity of nitrogen available to test the relief valves only results in "simmering" rather than "popping" of the valves. Thus a true relieving pressure cannot be determined with the relief valves in place on the reactors.

Current practice is to remove the relief valves from the reactors and to send them to a relief valve repair shop for testing, inspection and reworking. The rework includes disassembly, cleaning and replacing/refurbishing internal parts as required so that the relief valve meets the original manufacturers specifications.

Initially, all reactor relief valves will be sent to a relief valve repair shop on a scheduled basis. The valves will be disassembled, cleaned and refurbished as necessary. The set pressure on each of the relief valves will also be increased approximately 10 psi while at the repair shop.

After the initial testing and refurbishing, the valves will be reinstalled on the reactors. The information obtained on valve condition versus period of time between the rework will be analyzed. From this data, a decision on the frequency of testing and refurbishing the valves will be established.

VII. RELIEF VALVES - Continued

A. Reactor Relief Valves - continued

All new reactor relief valves purchased will be pretested by the manufacturer. Upon installation, the relief valves will be removed and tested at a relief valve shop per the frequency established above.

B. Other Relief Valves in Vinyl Chloride Service

Relief valves in the vinyl chloride service, except those on the reactors, will be tested and refurbished at either a relief valve repair shop or by the plant maintenance personnel. The frequency of testing and refurbishing will be established by the plant maintenance department.

C. Recordkeeping

The maintenance department shall keep a record of all tests and repairs made on the relief valves.

RUPTURE DISC CHECK-IN

DATE RECEIVED	LOT NUMBER	STOCK NUMBER	DISC SIZE	DESIGN PRESSURE A 72°F	NUMBER OF DISCS	LOT INSPECTED BY	DESTRUCTIVE TEST REQUIRED*	LOT APPROVED (YES, NO)	COMMENTS

* All rupture discs in VCI service.

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REACTOR _____

RUPTURE DISC

Disc Removed

Date Removed _____

Specific Location _____

Lot No. _____

Burst Pressure at 70°F _____

Burst Pressure at Higher Temp. _____

Disc Size _____

Destructive Test Burst Pressure _____

Holder No. _____

Individual(s) Removing Disc _____

Individual(s) Performing Destructive Test _____

Reason for Removal _____

Disc Installed

Date Installed _____

Specific Location _____

Lot No. _____

Rated Burst Pressure at 70°F _____

Rated Burst Pressure at Higher Temperature _____

Disc Size _____

Tested to 90°F By _____

Test Observed By _____

Installed on Reactor By _____

Installation on Reactor Observed By _____

Holder No. _____

Stock No. _____

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TABLE I

RUPTURE DISCS IN VCM SERVICE

AVAILABLE AT THE PLANT

A

ATTACHMENT B

DATE / TIME	LEAK NO. (S)	QC STREAM LOCATION / LEAK LOCATION	QC READINGS / HNU READINGS	REPAIRS MADE	DATE OF REPAIRS / REPAIRED BY	REPAIR VERIFIED BY

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A

ATTACHMENT C

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To: H. D. Garrison, PVC Plant, Oklahoma City

From: E. L. Sones, Research and Development, Ponca City
Date: July 24, 1985

VISTA

Interoffice Communication

Subject: **ASR-01-85-6849-01 - EVALUATION OF THE HEWLETT-PACKARD 19395A HEADSPACE ANALYZER**

On July 10, 1985, a Hewlett-Packard System for heated-headspace analyses by gas chromatography was installed at the Oklahoma City PVC Plant for our evaluation. After a brief period of familiarization and some optimization of conditions, I began a study using known samples to allow objective conclusions to be made regarding the accuracy and precision of the HP19395A system and its potential to replace the Perkin-Elmer F-42 system which you currently use for VCM determinations.

Replicate blended samples of VCM in wetcake, resin and water were prepared in concentrations which spanned the respective ranges of interest for each sample type. The samples were then divided and a set of each were analyzed by both headspace systems per the EPA Method 107 procedure.

The Hewlett-Packard system using the 19395 headspace sampler and the H-P 5890 gas chromatography provided both excellent accuracy and precision on all three types of samples. In all cases the H-P proved better than your P-E F-42 analyzer for both precision and accuracy.

The resulting data are plotted against the theoretical concentrations in Figures 1 through 4 by sample type and analyzer system. These data are also compared to the known values using linear regression, and a summary is in Table I.

This evaluation was specifically designed to provide known samples whose concentrations were calculated independently of the accuracy of the calibration gases and the assumptions involved in the equations in Method 107. The procedures for sample preparation and analyses are in Appendix I. Detailed data are in Appendix II.

Features of the Hewlett-Packard system which are attractive include:

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1. The external pressurization of the sample vial prior to analysis is an optional step and the chosen pressure is independent of the GC column headpressure. Therefore the whole subject of prepressurization of vials is not germane to this injection technique.

2. There are few moving parts and the modular nature of the system will allow for easier repair or exchange of failed parts.

3. The system uses a standard gas chromatograph with flame ionization detectors for analysis. Any similar GC will give equivalent data and the GC can easily be used for analyses requiring liquid injections.

4. The cost of the system is very attractive compared to the Perkin-Elmer HS-100, the alternative analyzer to replace the F-42.

Detracting features of the H-P system include:

1. Only 24 vials can be processed at a time compared to 30 vials for the F-42 and 100 for the HS-100.

2. The system is not designed to allow additional samples to be added to a set once analysis has begun.

The H-P 19395A system provides better accuracy, precision, and sensitivity than obtained with the P-E F-42 system. While the H-P 19395A is not specifically approved by Method 107, the H-P system has been shown to provide excellent VCM analyses and approval as an equivalent analyzer should be no problem. With these considerations and the cost factor, the Hewlett-Packard system is my recommended replacement for the P-E F-42.

E. L. Sones
Engineering Research

cwj

Attachments

cc: JPW, MGJ, RP, RLP, JEY, PLF, DSC, JCL

References: Research Notebook V0183, Pages 54-75

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TABLE I

COMPARISONS OF EXPERIMENTAL VCR DETERMINATIONS WITH THEORETICAL CONCENTRATIONS

For Wetcake Samples

	Hewlett-Packard		Perkin-Elmer
	7/12/85	7/15/85	7/15/85
# Samples	14	16	16
Slope	1.0356	1.0714	1.2342
Intercept	- 1.5	- 4.9	- 6.6
Corr. Coeff.	0.99932	0.99987	0.9869

For Water Samples

	Hewlett-Packard	Perkin-Elmer
# Samples	8	8
Slope	0.9988	1.1171
Intercept	0.21	0.79
Corr. Coeff.	0.99928	0.9788

For Resin Samples

	Hewlett-Packard	Perkin-Elmer
# Samples	8	8
Slope	1.0149	1.2758
Intercept	0.06	0.06
Corr Coeff.	0.99958	0.9955

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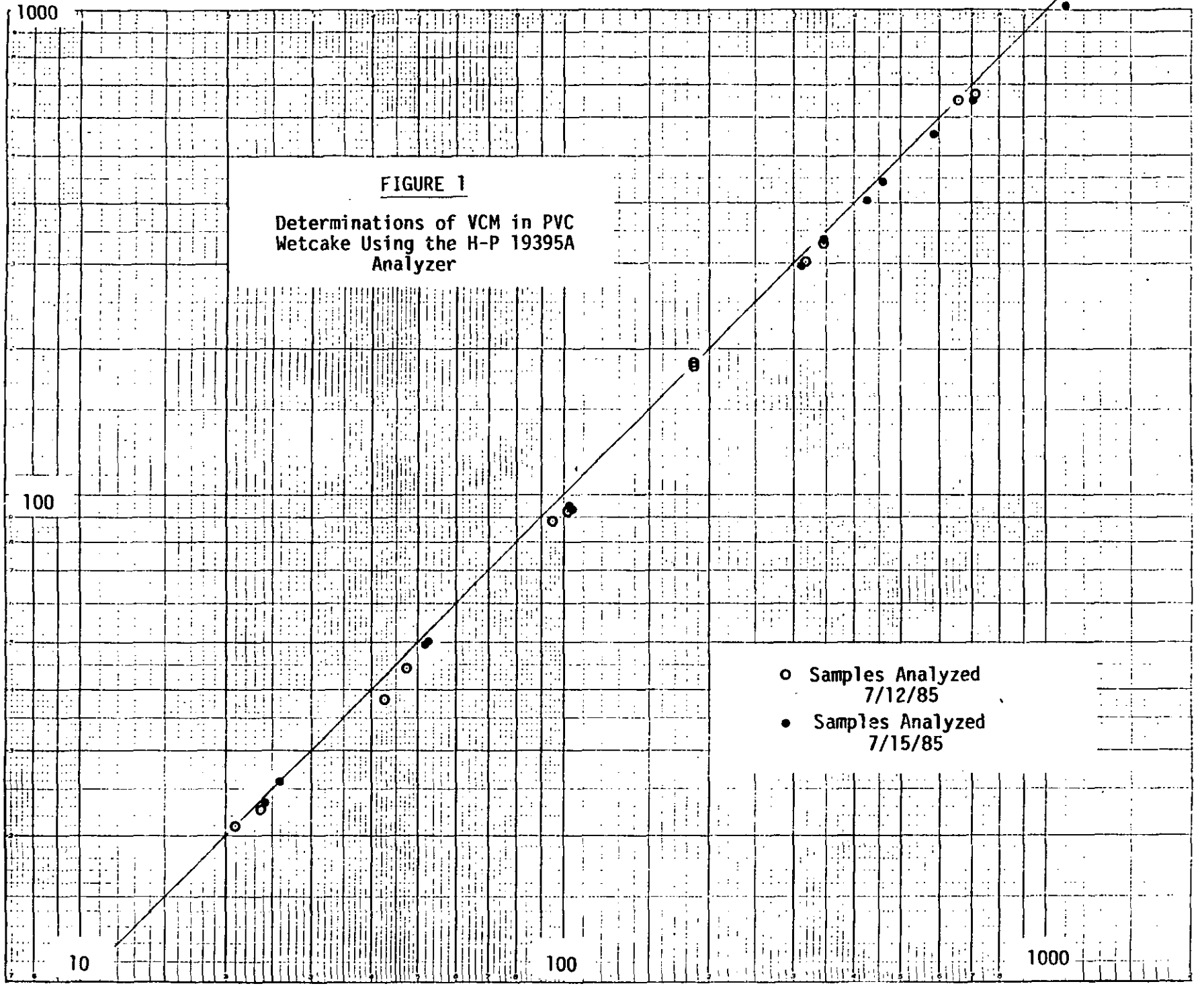

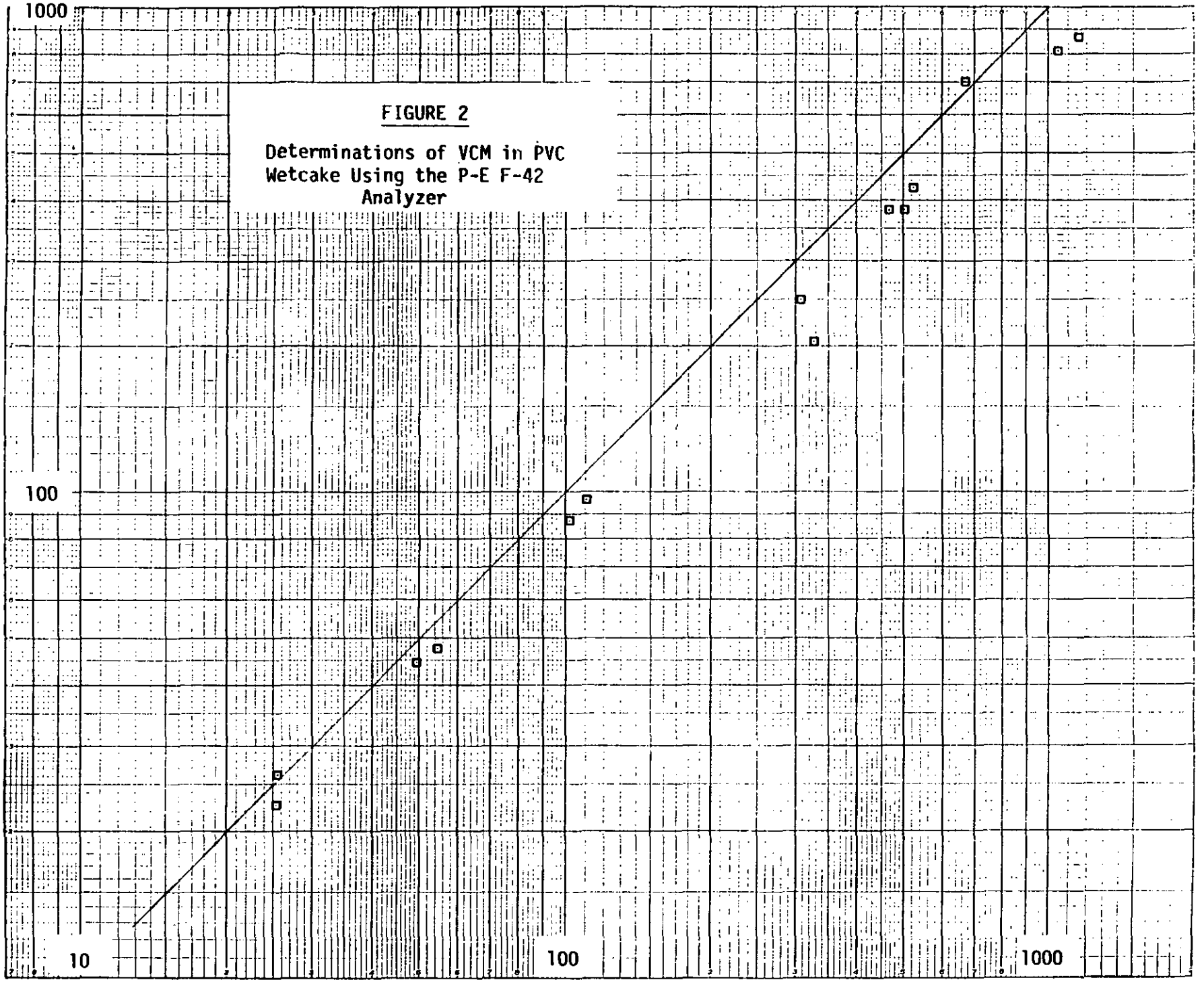

FIGURE 2

Determinations of VCM in PVC Wetcake Using the P-E F-42 Analyzer

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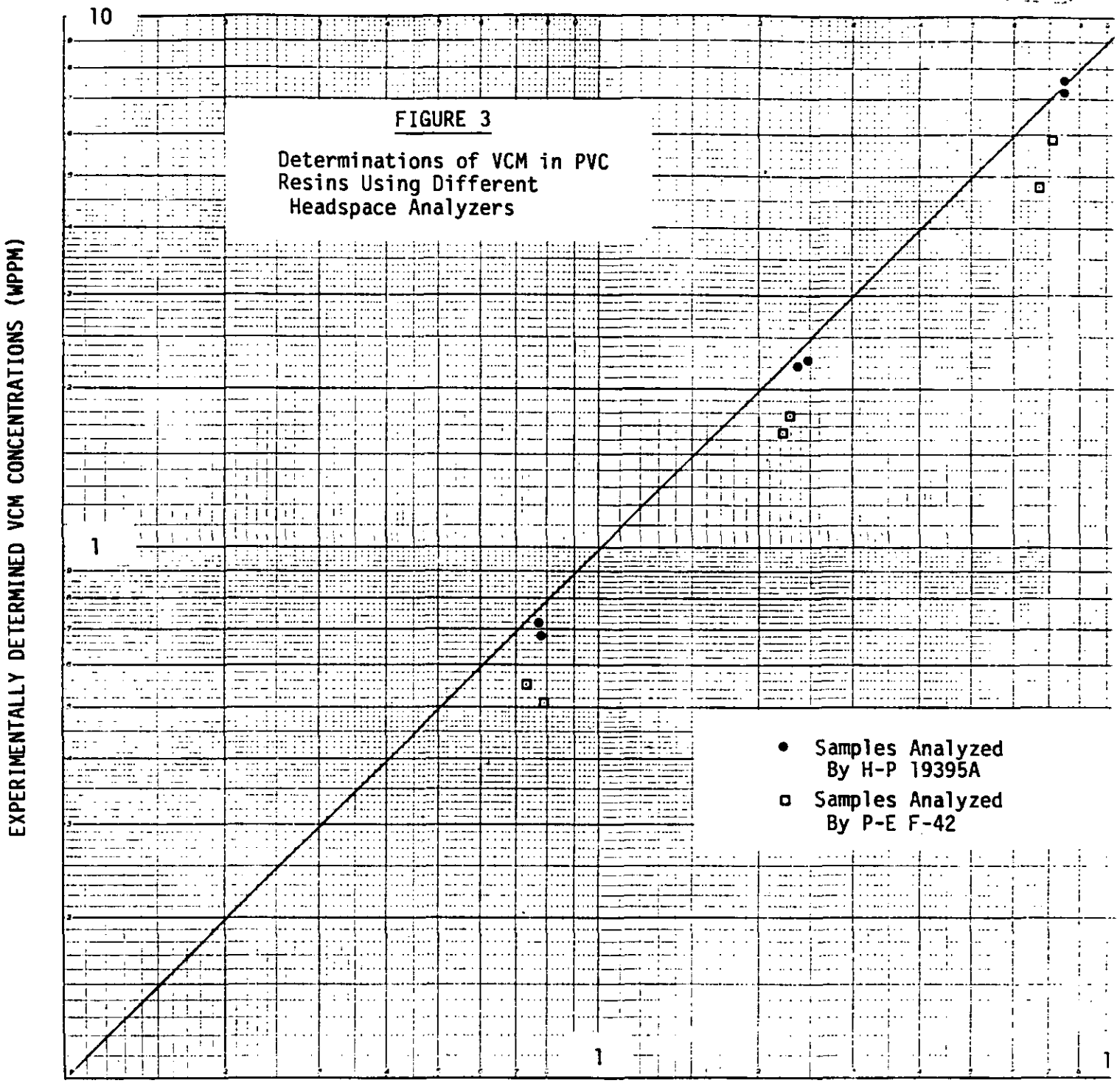

FIGURE 3

Determinations of VCM in PVC Resins Using Different Headspace Analyzers

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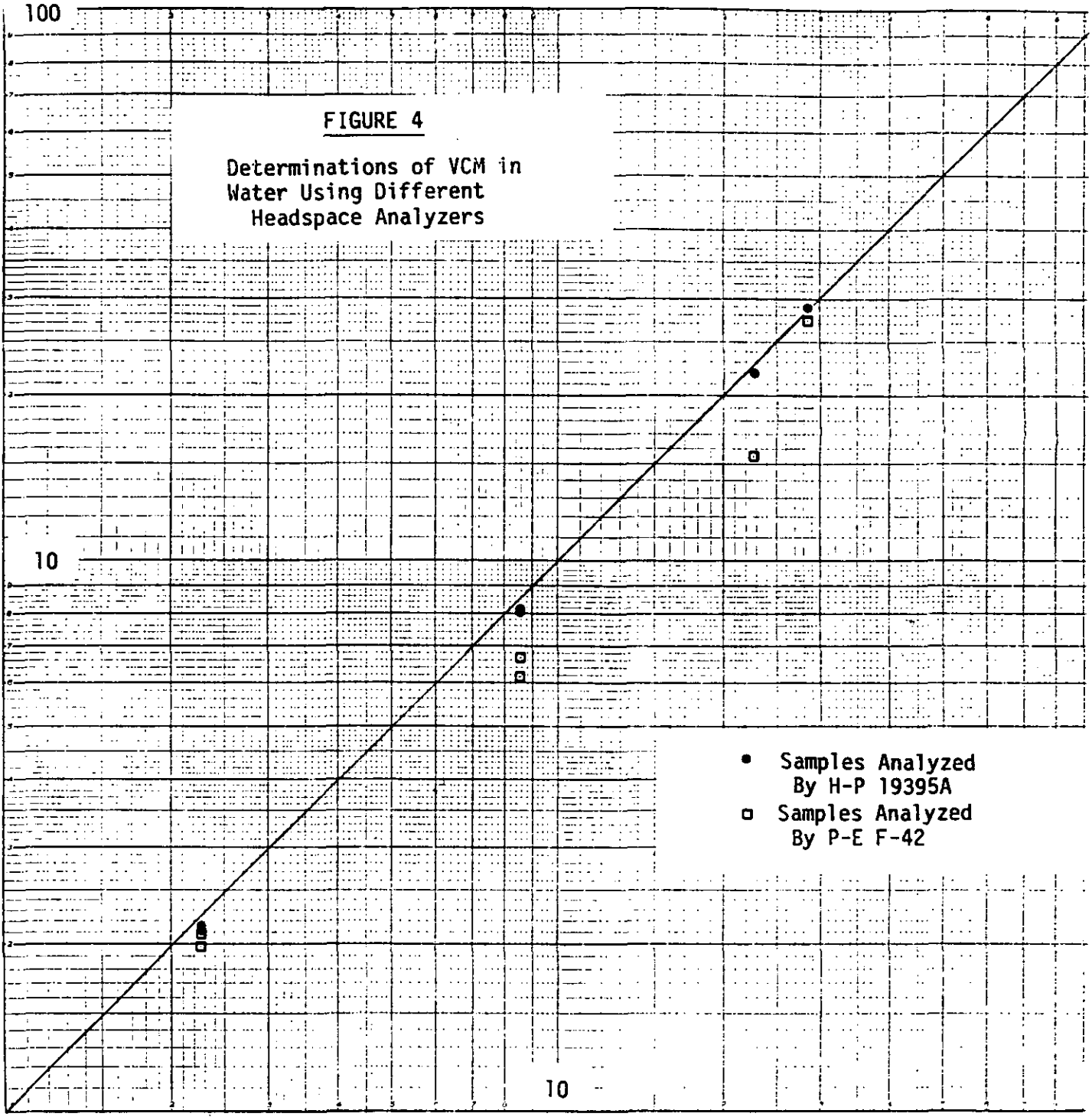
FIGURE 4

Determinations of VCM in Water Using Different Headspace Analyzers



EXPERIMENTALLY DETERMINED VCM CONCENTRATIONS (WPPM)

ACTUAL VCM CONCENTRATIONS (PARTS PER MILLION BY WEIGHT)

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APPENDIX I

Procedure for Preparation of Known PVC Wetcake Samples

Each sample was individually prepared by the following steps:

1. A clean, unused headspace vial (Shamrock Glass Co., #778701) was tared on a top-loading balance (Mettler Model PL-1200) to 0.01 g.

2. Approximately one gram of a typical PVC resin (Vista 5385 resin from a retain of a 5/27/85 shipment) which was known to contain no detectable VCM was added by spatula and weighed to 0.01 g. (Note - This is a variance from EPA Method 107 in that weights were not read to 0.00001 g; however, there is no justification for requiring that degree of accuracy in this method.)

3. Using a calibrated, 1-mL syringe (Becton - Dickinson Model 2004) and a 20-gauge needle, exactly 0.60 g of water (HPLC grade) was added to the resin.

4. The vial was sealed with a butyl-rubber septum and aluminum retainer ring.

5. A known volume of VCM gas (99.9% from Ideal Gas Products) at laboratory temperature and pressure was injected into the vial using one of the following syringes:

   a) Precision Sampling Model 8-110 Syringe of 10 uL capacity, measured to deliver 1.16 uL per nominal uL, was used for the low concentrations.

   b) Hamilton Model 705 syringe of 50 uL capacity, measured to deliver 0.992 uL per nominal uL, was used for middle-range concentrations.

   c) Precision Sampling Model 306000 syringe of 0.5 mL capacity, measured to deliver 0.9994 uL per nominal uL, was used for high concentrations.

Fourteen wetcake samples (V183-55 series) were prepared and analyzed on 7/12/85 using the H-P system. Thirty-two wetcake samples (V183-61-S series) of eight concentrations were prepared on 7/15/85. Two vials of each concentration were randomly picked for analysis on the H-P system and the remainder were analyzed on the P-E system on that same day.

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Procedure for Preparation of Known PVC Resin Samples

Each sample was individually prepared by the same procedure as used to prepare PVC wetcake samples with the following exceptions:

1. Approximately four grams of the same PVC resin was used per sample.

2. Only 100 uL of the same water was added per sample.

3. All VCM volumes were injected using the Precision Sampling Model B-110 syringe.

Sixteen resin samples (V183-61-R series) of four concentrations were prepared on 7/15/85. Two vials of each concentration were randomly picked for analysis on the H-P system and the remainder were analyzed on the P-E system on the same day.

Procedure for Preparation of Known Water Samples

Each sample was individually prepared by the same procedure as used to prepare PVC wetcake samples with the following exceptions:

1. No PVC resin was added.

2. Exactly 1.00 g of the water (HPLC grade) was added using the calibrated, 1-mL syringe.

3. All VCM volumes were injected using the Precision Sampling Model B-110 syringe.

Sixteen water samples (V183-61-W series) of five concentrations were prepared on 7/15/85. Vials of each concentration were randomly picked for analysis on the H-P system and the remainder were analyzed on the P-E system on the same day.

Procedure for Preparation of Standard Gas Samples

Each vial was filled with known concentrations of VCM-in-nitrogen gas per EPA Method 107 with the following notations:

1. The standard gases were manufactured by Ideal Gas Products, Edison, NJ, and shipped with all required certifications.

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2. Data on the cylinder standards are:

   3708 vppm in Cylinder K105906, Expiration 11/26/85
   2149 vppm in Cylinder 72948, Expiration 8/23/86
   523 vppm in Cylinder S180995, Expiration 8/23/86
   54.8 vppm in Cylinder H25891, Expiration 4/22/87

3. The cylinders were set at a discharge pressure of 15 psig which has been shown to deliver approximately 600 mL/min of gas through the 1/8" O.D. steel sample lines.

4. Each vial was purged at least 90 seconds with the appropriate gas prior to sealing.

5. After sealing, 100 µL of the water was injected into each vial using a Hamilton Model 710N syringe with a 100 µL capacity and a 22-gauge needle.

Two sets of the four standard gases were analyzed with each set of samples to obtain a calibration curve for that set.

Instrumental Conditions For the Hewlett-Packard System

1. The GC column is 0.2% Carbowax 1500 on Carbopak C (60/80 Mesh) in 2M x 1/8 in. O.D. stainless steel. The column was held at 60°C isothermally with a total nitrogen carrier flow of 28 mL/min with 8 mL/min flow through the Model 5890 GC inlet and 20 mL/min through the Model 19395A sample line. The nitrogen supply was regulated at 60 psig; the nitrogen at the Model 19395A was regulated at 1.4 bar; and the nitrogen through the flow controller on the GC gave a total column headpressure of 161 kPa.

2. The FID oven was run at 150°C with the H_2 supply at 26 psig and air supply at 51 psig. The input range was 8 on 7/12/85 and 7 on 7/15/85.

3. The inlet on the Model 5890 GC was set at 100°C.

4. The headspace method conditions were 0 min equilibration time, 90°C bath temperature, 92°C loop temperature, 3 min intervals between sample injections, and single injections from each vial.

5. The headspace probe program was probe entry at 1 second, pressurization at 1.0 bar from 2-3 seconds, loop venting from 4-9 seconds, injection from 10-20 seconds, and probe withdrawal at 21 seconds.

6. Each set of samples were conditioned in the 90°C bath from 65-80 minutes prior to analyzing the first sample. No sample was conditioned longer than 140 minutes.

7. The H-P Model 3390 integrator was set with a peak width of 0.04 minutes, a threshold of 0, and an area rejection of 0. VCM eluted in 68 sec.

8. The Model 5890 GC we had available did not have a backflush valve. That capability is needed for routine analyses.

Instrumental Conditions for the Perkin-Elmer F-42 System

1. The GC column is 0.2% Carbowax 1500 on Carbopak C (60/80 mesh) in 2 M x 1/8" O.D. stainless steel tubing. The column was held at 60°C isothermally with a nitrogen carrier flow regulated at 1.0 bar to give 26 mL/min through the column.

2. using the equation to calculate pressurization pressure in EPA Method 107 for P_1 = 200 kPa absolute, the value is 100 kPa absolute which is atmospheric pressure. Therefore no vial pressurization step was necessary.

3. The FID was operated at 150°C with H_2 supply at 0.7 bar and air supply at 1.3 bar. The input range was at 1.

4. The GC inlet was at 150°C and the headspace needle unit at 150°C.

5. The Haake Model N3 thermobath was controlled at 90.5°C with water heat transfer fluid.

6. The injection time was 3 seconds; analysis time was 2.0 minutes; backflush began at 2.0; and the stabilization time was 1.0.

7. The Perkin-Elmer Model M-1 integrator had Slope Sens = 00200, Baseline Test = 00005, T1 = 40, Plateau Test = 00010, and T4 = 230.

8. Each sample was conditioned in the bath for at least 60 minutes and no more than 140 minutes before analysis.

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Calculations for Determination of VCM Concentrations

1. For each set of samples analyzed, eight standard gases were also determined. From the resulting eight VCM area measurements at four concentrations, a slope, m, and intercept, b, and a correlation coefficient, R, were calculated by linear regression.

2. The headspace VCM concentration, C^1 in vppm, for each sample in that set was then calculated by

$$C^1 = mA + b$$

where m = slope of calibration curve,
b = intercept of calibration curve, and
A = area of VCM peak in sample

(A second concentration, C^0, was also calculated for each sample with b = 0.)

3. For each sample, the gaseous volume of the vial, Vg in mL, was calculated by the following equation:

$$Vg = 22.3 - \frac{WF}{1.36} - \frac{W(1-F)}{0.965}$$

where 22.3 = the total volume of a sealed vial in mL
W = sample weight in grams
F = weight fraction of PVC solids in sample
1.36 = density of PVC at 90°C
0.965 = density of water at 90°C

4. For each sample, the VCM concentration in parts per million by weight, C_{RVC}, was calculated by the following equation:

$$C_{RVC} = \frac{C^1 Pa}{F T_1}\left[\frac{M Vg}{RW} + Kp FT_2 + Kw T_2 (1-F)\right]$$

where Pa = ambient atmospheric pressure in mm Hg,
T_1 = lab temperature in °K,
M^1 = molecular weight of VCM = 62.5
R = gas constant = 62360 mL - mm Hg/mole - °K
Kp = Henry's Law Constant for VCM in PVC at 90°C = 6.52 x 10-6,
Kw = Henry's Law Constant for VCM in water at 90°C = 7×10^{-7}, and
T_2 = equilibration temperature = 363°K

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(For water samples, F is set at 1.0 for this equation.)

5. For each sample, a second calculation of VCM concentration was performed using C^0 instead of C^1 in the above equation.

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APPENDIX II

Blended PVC Wetcake Samples Analyzed 7/12/85 on the H-P System

Sample #	Sample Weight	Fraction Solids	VCM Area	Blended VCM Conc[1]	Experimental VCM Conc[2]
V183-55-5	1.74	0.655	739	0.0	2.0
6	1.72	0.651	181580	22.0	23.0
7	1.64	0.634	354720	47.3	46.2
8	1.56	0.615	712550	102	97.7
9	1.66	0.639	1504800	186	185.7
10	1.74	0.655	2892000	345	332.1
11	1.70	0.647	5691800	716	673.5
14	1.72	0.651	5655600	659	658.3
15	1.76	0.659	2690700	318	304.2
16	1.66	0.639	1528900	186	188.6
17	1.64	0.634	708780	94.6	90.2
18	1.75	0.657	339190	42.8	40.3
19	1.64	0.634	182060	23.7	24.7
20	1.70	0.647	1760	0.0	2.2

Pa = 728.4 mm Hg, T_1 = 299°K

Note 1 - Assumed VCM Density of 2.46 G/L

Note 2 - Used calibration curve with m = 0.0022515 and b = 38. The correlation coefficient for the calibration curve is 0.99969.

Blended PVC Wetcake Samples Analyzed 7/15/85 on the H-P System

Sample #	Sample Weight	Fraction Solids	VCM Area	Blended VCM Conc.	Experimental VCM Conc.[1]
V183-61-S-1A	1.87	.679	810	0.0	2.0
1D	1.59	.623	2870	0.0	2.7
2C	1.78	.663	431000	24.2	25.4
2D	1.70	.647	443260	25.9	27.8
3A	1.77	.661	916480	52.6	52.0
3C	1.78	.663	918160	52.1	51.7
4B	1.78	.663	1729000	104	95.5
4D	1.81	.669	1788800	102	96.4
5A	1.79	.665	5543500	310	299.1
5D	1.67	.641	5720500	345	340.3
6A	1.67	.641	7411900	460	440.2
6B	1.76	.659	7339100	424	404.8
7B	1.65	.636	9216700	586	557.0
7C	1.65	.636	10806000	703	652.7
8B	1.72	.651	17995000	1100	1022
8C	1.61	.627	18307000	1220	1145

Pa = 728.0 mm Hg, T_1 = 296°K

Note 1 - Used calibration curve with m = 0.0010885, b = 43, and r = 0.9986.

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Blended PVC Wetcake Samples Analyzed 7/15/85 on the P-E System

Sample #	Sample Weight	Fraction Solids	VCM Area	Blended VCM Conc.	Experimental VCM Conc.[1]
V183-61-S-1B	1.65	0.636	120	0.0	6.0
1C	1.59	0.623	80	0.0	6.3
2A	1.72	0.651	209060	25.5	32.1
2B	1.73	0.623	183650	25.3	28.7
3B	1.73	0.623	383870	54.4	53.8
3D	1.84	0.674	395230	49.6	50.7
4A	1.71	0.649	740230	111	100.3
4C	1.80	0.667	743390	103	93.6
5B	1.80	0.667	2104100	308	255.4
5C	1.73	0.653	1624500	327	209.8
6C	1.58	0.620	2673900	502	390.1
6D	1.65	0.636	2844500	469	388.9
7A	1.77	0.661	3499100	526	431.0
7D	1.70	0.647	5433200	671	706.0
8A	1.77	0.661	6669800	1050	817.5
8D	1.66	0.639	6522400	1160	875.3

Pa = 728.0 mm Hg, T_1 = 296°K

Note 1 - Used calibration curve with m = 0.002435, b = 108, and r = 0.9918.

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Blended Water And PVC Resin Samples Analyzed 7/15/85 on the H-P System

Sample #	Sample Weight	Fraction Solids	VCM Area	Blended VCM Conc.	Experimental VCM Conc.[1]
V183-61-W-1A	1.00	0.0	330	0.0	0.02
1C	1.00	0.0	340	0.0	0.02
2A	1.00	0.0	37110	2.28	2.11
2D	1.00	0.0	37510	2.28	2.14
3C	1.00	0.0	141250	8.56	8.05
3D	1.00	0.0	142830	8.56	8.14
4B	1.00	0.0	508890	28.5	28.99
4C	1.00	0.0	384870	22.8	21.92
V183-61-R-1B	4.06	1.0	1190	0.0	0.02
1D	3.63	1.0	1190	0.0	0.02
2B	3.71	1.0	35370	0.77	0.72
2C	3.68	1.0	33650	0.78	0.68
3A	3.61	1.0	107480	2.37	2.22
3C	3.47	1.0	106240	2.47	2.26
4B	3.74	1.0	379710	7.63	7.60
4C	3.83	1.0	364900	7.45	7.20

Pa = 728.0 mm Hg, T_1 = 296°K

Note 1 - Used calibration curve with m = 0.001074, b = 0, and r = 0.99983. If b = 39 is used, all experimental VCM concentrations increase by 2.0 wppm for water and 0.7 wppm for resin.

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Blended Water and PVC Resin Samples Analyzed 7/15/85 on the P-E System

Sample #	Sample Weight	Fraction Solids	VCM Area	Blended VCM Conc.	Experimental VCM Conc.[1]
V183-61-W-1B	1.00	0.0	0	0.0	0.00
1D	1.00	0.0	0	0.0	0.00
2B	1.00	0.0	15340	2.28	1.98
2C	1.00	0.0	16280	2.28	2.10
3A	1.00	0.0	47950	8.56	6.19
3B	1.00	0.0	51350	8.56	6.63
4A	1.00	0.0	211900	28.5	27.37
4D	1.00	0.0	119400	22.8	15.42
V183-61-R-1A	4.06	1.0	140	0.0	0.01
1C	4.12	1.0	120	0.0	0.01
2A	3.91	1.0	12430	0.73	0.55
2D	3.62	1.0	10840	0.79	0.51
3B	3.88	1.0	37270	2.21	1.65
3D	3.74	1.0	39170	2.29	1.78
4A	4.25	1.0	116060	6.71	4.79
4D	4.05	1.0	136160	7.05	5.83

Pa = 728.0 mm Hg, T_1 = 296°K

Note 1 - Used calibration curve with m = 0.002435, b = 0, and r = 0.9918. If b = 108 is used, all experimental VCM concentrations increase by 5.7 wppm for water and 1.80 wppm for resin.

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ATTACHMENT D

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Conoco Chemicals Company
Division of Conoco Inc.
P.O. Box 91, New Highway 25
Aberdeen, MS 39730

Route: _____

Copy: _____

File: _____

X-F: _____

February 26, 1980

Mr. Tommie A. Gibbs
Chief, Air Engineering Branch
Region IV
United States Environmental Protection Agency
345 Courtland Street, N.E.
Atlanta, GA 30308

Dear Mr. Gibbs:

Test Method 107 included in Appendix B of 40CFR, Part 61, Subpart F, requires a polyvinyl chloride slurry sample to be run within 24 hours of the time the sample is taken (7.2). The results of the attached Conoco Technical Service Report No. 427-79-849-1 show there is no significant loss of residual VCM in PVC slurry samples analyzed up to 5 days after the sample is taken. Based on the results of this study, we are asking approval of an alternate procedure which requires slurry samples to be run within 5 days of sampling rather than 24 hours specified in Appendix B, paragraph 7.2 of the standard.

Conoco R & D personnel have discussed this change with Research Triangle. The Research Triangle personnel stated the 24 hour limit appears in the Standard because tests had not been conducted to determine if slurry samples could be held for longer times without loss of VCM. They suggested we perform the test, and if no VCM loss occurred with the longer hold to them, request the approval of the alternate procedure from the Regional Office.

We request approval of the alternate procedure to prevent violations to the Standard if we have minor problems with the Perkin-Elmer Corporation Model F-42 head space analyzer which could delay slurry analysis longer than 24 hours after sampling and for other reasons that could necessitate longer slurry hold times before analysis.

Please direct any questions you may have concerning this request to me at 601-369-8111, ext. 239.

Sincerely,

R. A. Frohreich
Chief Process Engineer

jf

Attachment
c: CLM

conoco

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Technical Service Report

Continental Oil Company
Research and Development Department
Analytical Research Section
Ponca City, Oklahoma

Report No. 427-79-849-1

To Gregory J. Husen

From Jana L. Florea and Richard E. Laramy

Date June 13, 1979

Subject EPA VARIANCE STUDY: THE EFFECT OF SAMPLE STORAGE TIME ON RESIDUAL VCM CONTENT OF PVC WETCAKES

Object The objective was to conduct a study to determine if PVC wetcake samples can be stored for longer than 24 hours without loss of VCM. If the data showed no loss of VCM, they would be used to request a variance from EPA on the mandatory 24-hour limit for analysis after sampling.

Conclusion

The study showed that there was no significant loss of residual VCM as the PVC wetcake samples were held over the five days of the study.

Introduction

The samples were collected and prepared at the Oklahoma City PVC Plant October 2, 1978. Samples of PVC slurry were collected in 8-oz bottles by plant personnel in rapid succession during a reactor dump so that they would all represent the same sample. Using these bottles of slurry, wetcake samples were prepared in F-42 Automatic Headspace Analyzer vials with septum tops. Five wetcake samples and three samples for total solids determinations were obtained from each 8-oz bottle of slurry. The three total solids determinations were averaged and used to calculate the residual VCM content of the corresponding five wetcake samples that were prepared from the same slurry bottle. Five of these prepared wetcake samples were analyzed for residual VCM using an F-42 Automatic Headspace Analyzer in the Oklahoma City plant each day for five days.

Experimental Conditions

The method as prescribed by EPA for determining residual VCM in PVC slurry (EPA Method 107, Federal Register, Vol. 41, No. 205, October 21, 1976, and amendment in the Federal Register, Vol. 42, No. 109, June 7, 1977) requires that PVC wetcake be analyzed within 24 hours after sampling, using a Perkin-Elmer F-42 Automatic Headspace Analyzer. The method presently being used in the Oklahoma City plant lab was adopted directly from EPA Method 107 (TM No. 604-78-849-1). The wetcake sample is equilibrated in a constant temperature bath at 90°C for one hour. The VCM concentration in the headspace of the vial is determined by gas chromatography, using the F-42 and automatic injection, based on analyses of certified VCM cylinder standards. From a headspace concentration the sample concentration is calculated on a dry resin basis in parts per million by weight (wppm).

TABLE I. RESIDUAL VCM CONCENTRATIONS COLLECTED OVER FIVE DAYS

	Sample No.	Weight of Wetcake	Total Solids	wppm VCM	Mean
	1I	0.99	0.635	150.3	
	2II	1.11	0.625	159.3	
Day 1	3III	1.02	0.628	160.4	153.5
	6IV	1.12	0.625	143.6	
	2V	1.07	0.625	153.9	
	7I	1.07	0.623	179.3	
	6II	1.17	0.625	154.2	
Day 2	9III	1.15	0.618	164.6	171.3
	8III	1.14	0.632	178.9	
	13V	1.09	0.644	179.6	
	7V	1.03	0.623	190.7	
	9I	1.20	0.618	161.8	
Day 3	4II	1.12	0.630	164.1	176.4
	15IV	1.13	0.640	179.4	
	11V	1.19	0.615	186.0	
	1V	1.06	0.635	144.8	
	13III	1.13	0.644	158.0	
Day 4	5IV	1.09	0.640	158.3	154.3
	10V	1.13	0.633	154.0	
	14IV	1.15	0.643	156.2	
	12V	1.20	0.628	166.7	
	12III	1.18	0.628	165.0	
Day 5	14I	1.13	0.643	153.2	163.6
	7II	1.07	0.623	176.3	
	6V	1.14	0.625	156.9	
				Average	163.8

The residual VCM concentrations obtained over the five-day period and the mean of these values for each day are shown, in wppm on a dry resin basis, in Table I.

Discussion

It should be obvious from the residual VCM concentrations given in Table I and the mean of these numbers for each day that the variance here is not in one direction, as you would expect if there was a loss of VCM over the five days. When a one-way analysis of variance is applied to the numbers shown in Table I, the following results are obtained:

TABLE II. ONE-WAY ANALYSIS OF VARIANCE FOR FIVE-DAY STUDY

Source	Sum of Squares	Degrees of Freedom	Mean Square
Day-to-day	2062.2	4	515.55
Within a day	1837.2	20	91.862
Total	3899.5	24	162.43

Snedecor's variance ratio F test on the day-to-day variance estimate shows that there is a significant difference in the day-to-day values, using the variance within a day as the random error (515.55/91.862 = 5.61, which is greater than 2.87). The 2.87 value is taken from a table of F values at the 5% level of variance ratio (95% confidence level) with 4 degrees of freedom for the greater and 20 degrees of freedom for the lesser variance estimate. Again this large day-to-day variance is indicative of the day-to-day reproducibility of the method and not of a loss of VCM over the five days, as pointed out using Table I. The standard deviation for the five means shown in Table I is 10.14. This point is further verified when the reproducibility within a day is examined. The standard deviation of each of the five days, from Day 1 to Day 5, is 6.89, 11.49, 12.94, 5.56, and 9.03, respectively. This variation within a day is almost equal to the day-to-day variation.

In conclusion, and in support of a variance on the 24-hour sample storage limit, there was no loss of residual VCM from the wetcake samples over a five-day period. The day-to-day reproducibility in the study was shown to be significant statistically but not in one direction as you would expect with a loss of VCM.

References

Technical Service Report No. 440-78-849-1
Technical Memorandum No. 604-78-849-1

Jana L. Florea

Jana L. Florea
Associate Chemist
Analytical Research Section

R. E. Laramy

R. E. Laramy
Research Group Leader
Separations Analysis Group
Analytical Research Section

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IV
345 COURTLAND STREET
ATLANTA, GEORGIA 30308

CONFIDENTIAL

APR 8 1980

REF: 4AH-AF

Mr. R. A. Frohreich
Conoco Chemicals Corporation
Division of Conoco, Inc.
P. O. Box 91, New Highway 25
Aberdeen, Mississippi 39730

Dear Mr. Frohreich:

This office has received your letter of February 26, 1980 concerning your request to be allowed to use an alternate method to the analysis procedures for poly vinly chloride slurry concentration determination as described in the EPA Test Method 107 (See Appendix B of 40 CFR 61, Subpart F).

We are reviewing the research data provided by your company and will give you our determination in the near future.

If you have any questions in this matter please contact Mr. Joe Riley of my staff at 404/881-2786.

Sincerely yours,

Tommie A. Gibbs

Tommie A. Gibbs
Chief
Air Facilities Branch

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IV
345 COURTLAND STREET
ATLANTA, GEORGIA 30308

AUG 19 1980

REF: 4AH-AF

Mr. R. A. Frohreich
Conoco Chemicals Corporation
Division of Conoco Inc.
P. O. Box 91, New Highway 25
Aberdeen, Mississippi 39730

Dear Mr. Frohreich:

As stated in my letter to you dated April 8, 1980, we have proceeded to review your request to use an alternate analysis procedure for determining vinyl chloride monomer (VCM) concentrations in polyvinyl chloride (PVC) slurry samples.

Because of the possible national impact our decision could have concerning a deviation from EPA's recommended test Method 107 of 40 CFR 61, Appendix 'B', Supart 'F', we have had to make a careful analysis of the technical service report No. 427-79-849-1 which was attached to your letter of February 26, 1980. Our conclusion is that we cannot, at this time, approve your proposed alternate method of analyzing the slurry samples at 5-day intervals (instead of within 24 hours as required by Method 107_X) based on the information provided to us in the above mentioned report. However, we suggest that another study be made using the following procedure:

1. Samples may be collected as before (many bottles collected in rapid succession).

2. Randomly choose five bottles from the whole set and prepare samples as before.

3. Store samples in a dark place refrigerated to 40°F.

4. For each day randomly choose one sample from each bottle (5 total samples per day).

5. Calculate wppm of VCM and mean for each day as before and perform a trend analysis test (such as Spearman's rank coefficient test) on the daily mean.

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AUG 19 1980

We feel that this approach will give us the data needed to make our decision in this particular situation.

Your cooperation in this matter is appreciated. If you have further questions, please contact Mr. Joe Riley of my staff at 404/881-2786.

Sincerely yours,

for Brian L Beals

Tommie A. Gibbs
Chief
Air Facilities Branch

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Conoco Chemicals Company
Division of Conoco Inc.
P.O. Box 91, New Highway 25
Aberdeen, MS 39730

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December 16, 1980

Mr. Tommie A. Gibbs
Chief, Air Engineering Branch
Region IV
United Stated Environmental Protection Agency
345 Courtland Street, N.E.
Atlanta, GA 30308

Dear Mr. Gibbs:

In my letter to you dated February 26, 1980, a request was made for approval of an alternate procedure for test method 107 of 40 CFR61, Appendix 'B', Subpart 'F'. The request was "to allow running of slurry samples up to 5 days of sampling," and was based on a study by Conoco. Your letter of August 19, 1980, stated the request could not be approved based on the data submitted, but suggested another study be conducted using the following procedure:

1. Samples may be collected as before (many bottles collected in rapid succession).

2. Randomly choose five bottles from the whole set and prepare samples as before.

3. Store samples in a dark place refrigerated to $40^{o}F$.

4. For each day randomly choose one sample from each bottle (5 total samples per day).

5. Calculate wppm of VCM and mean for each day as before and perform a trend analysis test (such as Spearman's rank coefficient test) on the daily mean.

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The analytical work you suggested has been completed by the anlaytical laboratory at this plant. A copy of the study is attached. The trend analysis test performed on the daily mean VCM concentrations shows no significant loss of residual VCM from wetcake samples held for up to five days before being analyzed. Spearman's rank coefficient test was used in the statistical analysis. The Spearman's rank coefficient determined for the test of the daily mean averages was 0.10. A coefficient of less than -0.90 would indicate a significant loss of VCM from the samples during the holding period. A copy of the test is attached.

Based on the results of this study, we are requesting the alternate procedure be approved which will allow slurry samples to be run within 5 days of sampling rather than within 24 hours as specified in test Method 107 of 40 CFR61, Appendix 'B', Subpart 'F'. This request is being made to prevent violation of the Standard if we have minor problems with the Perkin-Elmer or for other reasons that may necessitate longer slurry hold times before analysis.

Please direct any questions you may have concerning this request to me at 601-369-8111, extension 2239.

Sincerely,

R. A. Frohreich

R. A. Frohreich

c: Wayne Anderson - Mississippi Bureau of Pollution Control

bcc: CLM, RDJ, DSC - Aberdeen
J. J. Hall - Houston
J. Friend - Oklahoma City
R. J. Reusch, Jana Florea - Ponca City

Attachments

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Interoffice Communication

To R. D. Jackson

From D. S. Cox

Date December 12, 1980

Subject EPA VARIANCE STUDY: THE EFFECT OF SAMPLE STORAGE TIME ON RESIDUAL VCM CONTENT OF PVC WETCAKES

Object The objective was to conduct a study to determine if PVC wetcake samples can be stored for longer than 24 hours without loss of VCM. If the data showed no loss of VCM, they would be used to request a variance from EPA on the mandatory 24-hour limit for analysis after sampling.

Conclusion

The study shows there was no significant loss of residual VCM as the PVC wetcake samples were held over the five days of the study.

Introduction

The samples were collected and prepared at the Aberdeen Chemical Plant September 22, 1980. Twenty-three 8-oz bottles of 5385 PVC slurry were collected in rapid succession during a reactor dump from a D-300 reactor. The bottles were taken to the laboratory where five were randomly chosen from the set and placed in the refrigerator at 40°F to cool to room temperature. When the bottles had cooled sufficiently, the laboratory personnel prepared five wetcake samples from each of the five bottles. This involved filtering the slurry using a large Buchner funnel and weighing plugs of the resulting wetcake into F-42 vials for VCM analysis. The vials were then stored in the refrigerator at 40°F. A set of five vials, one from each of the five bottles, was analyzed each day for five days using the F-42 Headspace Analyzing Chromatograph according to EPA Method 107. After the 25 vials had been analyzed, a total solids was determined on each vial by drying each sample-plus-vial and recording the weight loss relative to the wet sample weight. The residual VCM concentrations in wppm on a dry weight basis obtained over the five-day period are shown in Table I.

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Experimental Conditions

The method as prescribed by EPA for determining residual VCM in PVC slurry (EPA Method 107, Federal Register, Vol. 41, No. 205, October 21, 1976, and amendment in the Federal Register, Vol. 42, No. 109, June 7, 1977) requires that PVC wetcake be analyzed within 24 hours after sampling, using a Perkin-Elmer F-42 Automatic Headspace Analyzer. The method presently being used in the Aberdeen Plant Lab was adopted directly from EPA Method 107. The wetcake sample is equilibrated in a constant temperature bath of 90°C for one hour. The VCM concentration in the headspace of the vial is determined by gas chromatography, using the F-42 and automatic injection, based on analyses of certified VCM cylinder standards. From a headspace concentration, the sample concentration is calculated on a dry resin basis in parts per million by weight (wppm).

Statistical Analysis

A trend analysis test was then performed on the daily mean VCM residual concentrations. Spearman's rank coefficient test was used. A Spearman rank coefficient of 0.10 was determined from the test of the daily mean averages. A coefficient of less than -0.90 would have indicated a significant loss of VCM from the samples during the holding period. Since no significant loss of VCM was determined, the conclusion reached is the holding of residual VCM samples up to five days before analyzing them is an acceptable procedure.

David S. Cox

David S. Cox

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Attachments

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TABLE I

RESIDUAL VCM CONCENTRATION OVER FIVE DAY HOLD PERIOD

	Sample Number	Weight of Wetcake Grams	Wetcake Weight % Solids	VCM Concentraction wppm VCM	Daily Mean wppm VCM
	A	1.507	64.0	72.95	
	B	1.480	64.9	72.77	
Day 1	C	1.445	64.8	69.51	71.88
	D	1.423	64.1	69.67	
	E	1.412	65.0	74.48	
	A	1.584	65.5	68.05	
	B	1.459	66.3	70.36	
Day 2	C	1.538	66.3	69.68	68.92
	D	1.455	65.4	66.59	
	E	1.384	65.9	69.94	
	A	1.535	67.2	70.36	
	B	1.544	67.9	73.20	
Day 3	C	1.386	67.8	70.90	71.55
	D	1.346	67.9	69.23	
	E	1.355	67.4	74.05	
	A	1.507	67.0	68.87	
	B	1.519	68.0	68.94	
Day 4	C	1.398	67.8	69.82	68.90
	D	1.354	68.2	65.70	
	E	1.356	68.1	71.19	
	A	1.568	67.2	71.68	
	B	1.563	68.1	73.05	
Day 5	C	1.450	68.4	73.76	72.61
	D	1.394	68.4	70.99	
	E	1.377	68.6	73.56	

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SPEARMAN'S RANK COEFFICIENT TEST

DAILY MEAN VCM RESIDUAL CONCENTRATIONS

Procedure is to rank daily means and then to square the difference of ranking.

Day	Daily Mean	Rank	Difference	Square Of Difference
1	71.88	4	-3	9
2	68.92	2	0	0
3	71.55	3	0	0
4	68.90	1	3	9
5	72.61	5	0	0

$$\text{Spearman's Rank Coefficient} = 1 - \frac{6 \Sigma d_i^2}{n^3 - n}$$

Where d_i^2 = square of differences
n = number of samples

$d_1^2 = 9$

$d_2^2 = 0$

$d_3^2 = 0$

$d_4^2 = 9$

$d_5^2 = 0$

$n = 5$

Then:

$$\text{Spearman's Rank Coefficient} = 1 - \frac{6(9+0+0+9+0)}{125 - 5} = 0.10$$

for $n = 5$, the critical value for significance is $\pm$ 0.90[1]

Therefore, since the calculated rank coefficient, 0.10 is less than the critical value, 0.90, there is no significant difference in the mean daily averages.

(1) Chemical Rubber Handbook Tables for Probability of Statistics Published by Chemical Rubber Company, 1966, page 330

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